Technical Report No. 32-679

The Ignition of Powdered Metals in Nitrogen and in Carbon Dioxide

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ABSTRACT

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The atmospheres of Mars and Venus are considered to consist essentially of mixtures of carbon dioxide and nitrogen. Experimental studies have shown that a number of powdered metals will ignite in carbon dioxide as well as in nitrogen. Metals shown to ignite in nitrogen are powdered lithium, beryllium, calcium, cerium, mischmetall, titanium, zirconium, thorium, and uranium. These metals will also ignite in carbon dioxide, in addition to the following, which ignite in carbon dioxide only: magnesium, aluminum, chromium, and manganese. The ignition temperatures for these metals are determined in order to develop appropriate fuels for use in the planetary atmospheres.

I. INTRODUCTION

In order to utilize the atmospheres of the planets Mars and Venus for propulsion, it is necessary to determine the properties of the atmospheres and then to find appropriate chemicals which will burn in these atmospheres. The guiding criterion for selecting a suitable propellant is the heat evolution per unit mass of propellant.

A recent estimate of the properties of the atmospheres of Mars and Venus is as follows: Venus—surface pressure, 7 atm; surface temperature, 700°K; composition (by volume), 85% CO_2, 10% N_2, 5% Ne; Mars—surface pressure, 25 mb; surface temperature, 300°K maximum; composition, 11% CO_2, 87% N_2, 2% Ar.

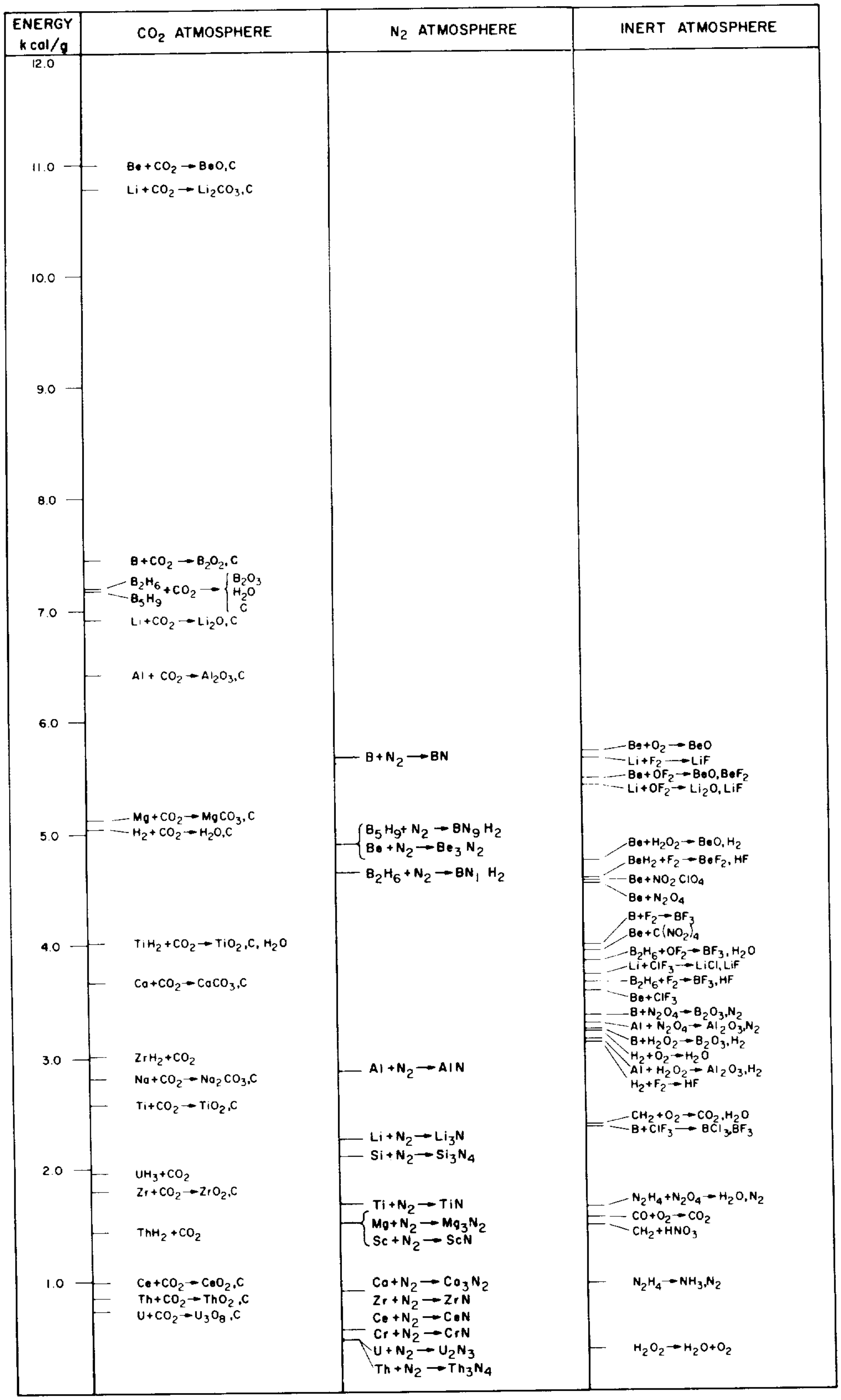

Fig. 1. Energy obtainable from propellants in atmospheres of nitrogen and of carbon dioxide, and in inert atmosphere (kcal/g)

The energy per unit mass of propellant is listed in Fig. 1 for the reaction with a N_2 atmosphere, for the reaction with a CO_2 atmosphere, and for the case in which the atmosphere is inert and the mass of propellant includes the sum of the mass of the fuel and the oxidizer. If the CO_2 or N_2 atmosphere is utilized, it is seen that the energy/mass ratio can be appreciably higher than for most bipropellant combinations.

II. EXPERIMENTAL PROCEDURE

This Report is concerned with finding the ignition temperature of some of the propellants listed in Fig. 1 in CO_2 and in N_2. The ignition temperature is measured by placing a chromel–alumel thermocouple in the fuel and heating the fuel in the gas. Ignition is easily seen as a virtually discontinuous temperature increase on a temperature–time graph, obtained by impressing the voltage output of the thermocouple on a strip-chart recorder input.

Several methods were used for heating the fuel in the gas. A tube furnace assembly is shown in Fig. 2, with the sample holder illustrated in Fig. 3. The crucible was filled with the fuel (in an Ar atmosphere for a highly pyrophoric fuel) and the sample holder placed on the furnace assembly. The system was evacuated and then filled with the gas. A flow rate of 100 ml/min was maintained, the furnace was turned on, and the rise of temperature with time was measured.

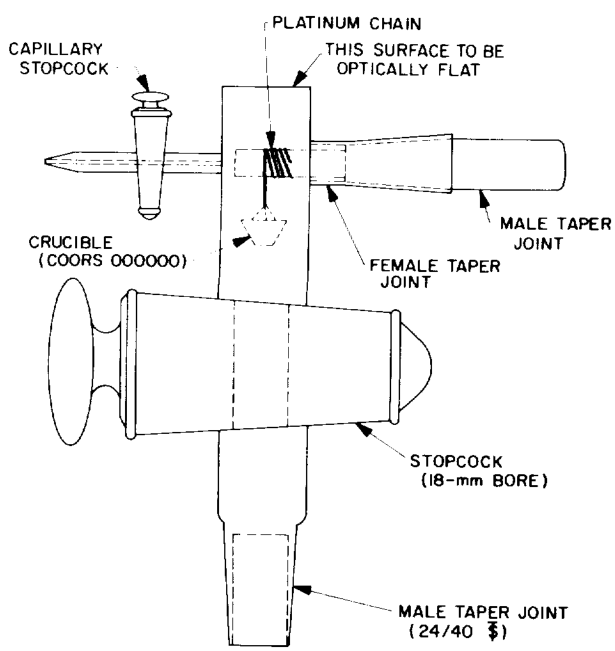

Fig. 2. Nitrogen ignition apparatus

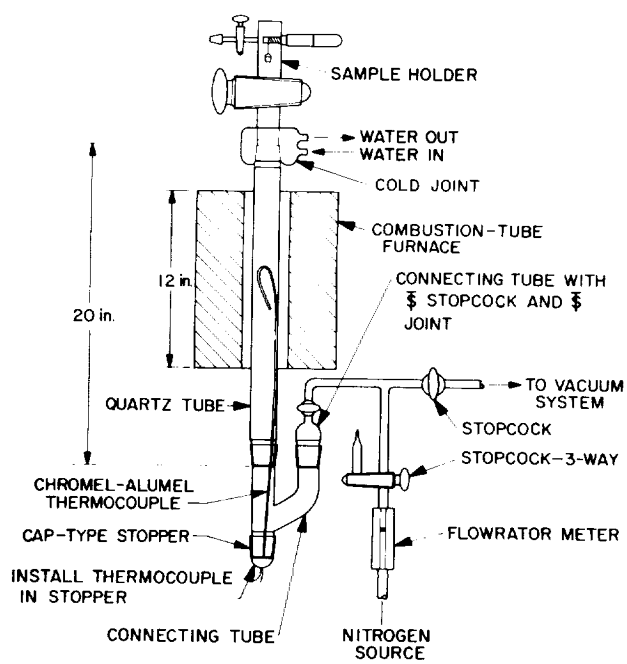

Fig. 3. Sample holder

Other ignition studies were performed in the tube reactor (Fig. 4), which was heated externally with a torch. The gas fuel rate was generally 100 ml/min through the tube. The powdered metal was put into a crucible, which was then placed at the bottom of the vycor tube, and the thermocouple was inserted into the powder. A similar reaction tube (Fig. 5) was used for the reaction with beryllium, and the pressure was maintained at 1 atm. The tube was heated in a sand bath.

The N_2 used in these experiments was Linde Co. Extra Dry High Purity, 99.995% pure, dew point $<-73°C$, <30 ppm O_2. The CO_2 was Matheson Coleman Grade, <100 ppm impurities.

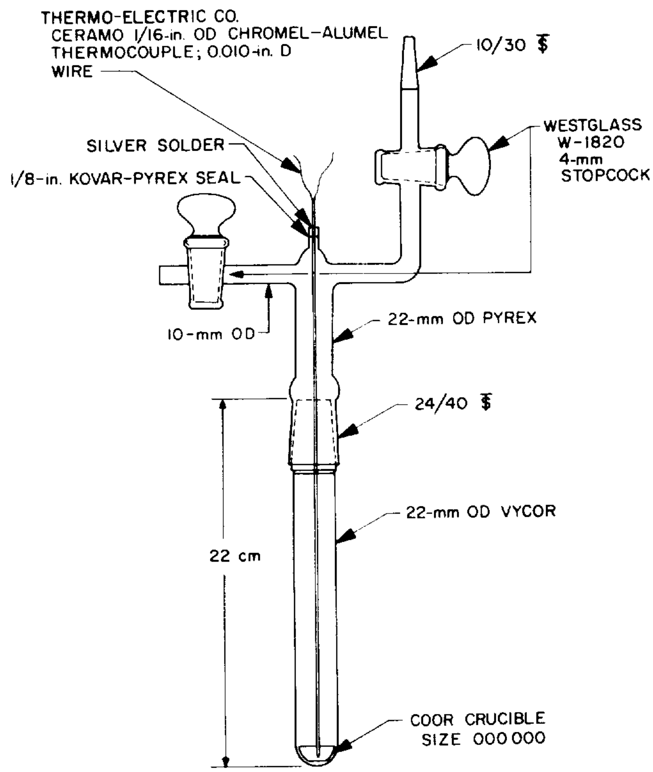

Fig. 4. Tube reactor

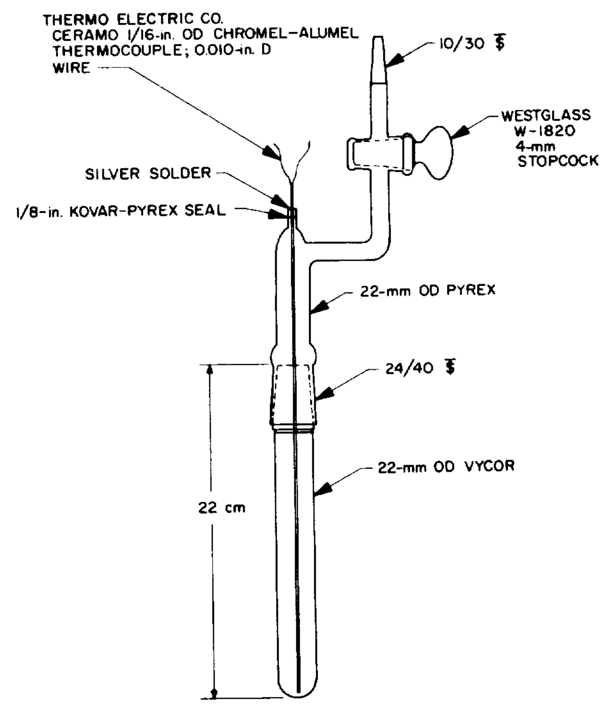

Fig. 5. Beryllium reaction tube

III. EXPERIMENTAL RESULTS

Lithium has been reported to ignite in N_2 at 170°C (Ref. 1), 450°C (Ref. 2), and at dull red heat (Refs. 3, 4). Here, powdered Li (Foote Mineral Co., New Johnsonville Operations, $\leq 100\mu$ particle size, lot No. 401-03) was heated in N_2 in the tube furnace apparatus (Figs. 6, 7) and, in two experiments, was observed to ignite at 388 and 410°C, respectively. In the tube reactor (Fig. 8), the Li was seen to ignite at 330°C in CO_2.

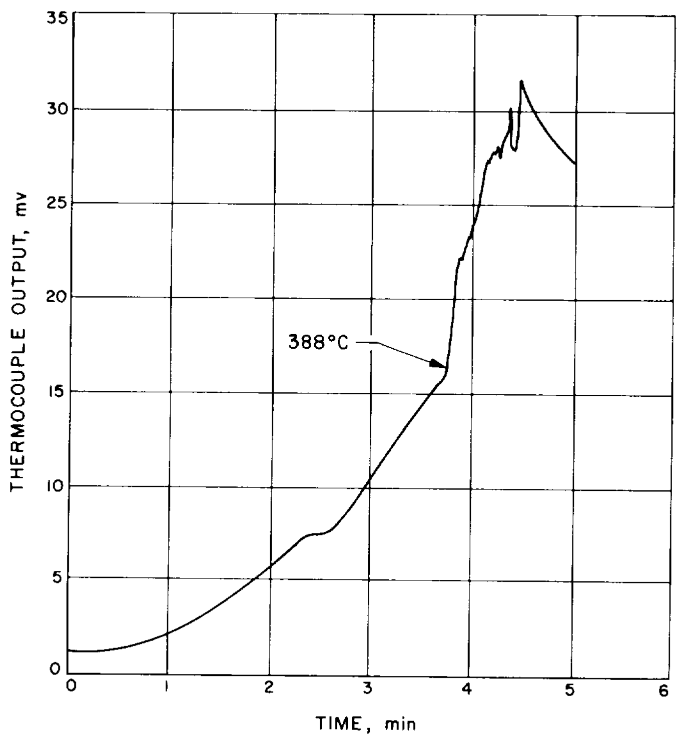

Fig. 6. <100μ lithium + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 388°C

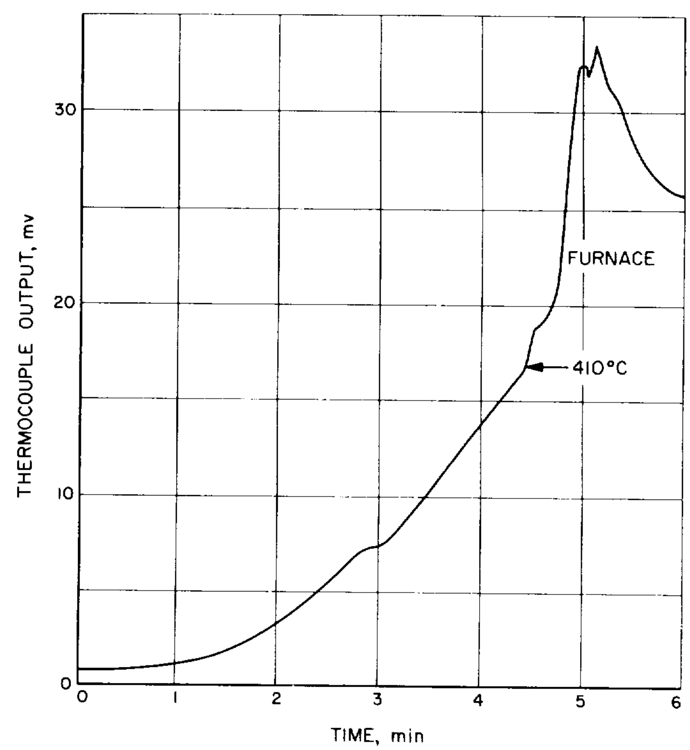

Fig. 7. <100μ lithium + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 410°C

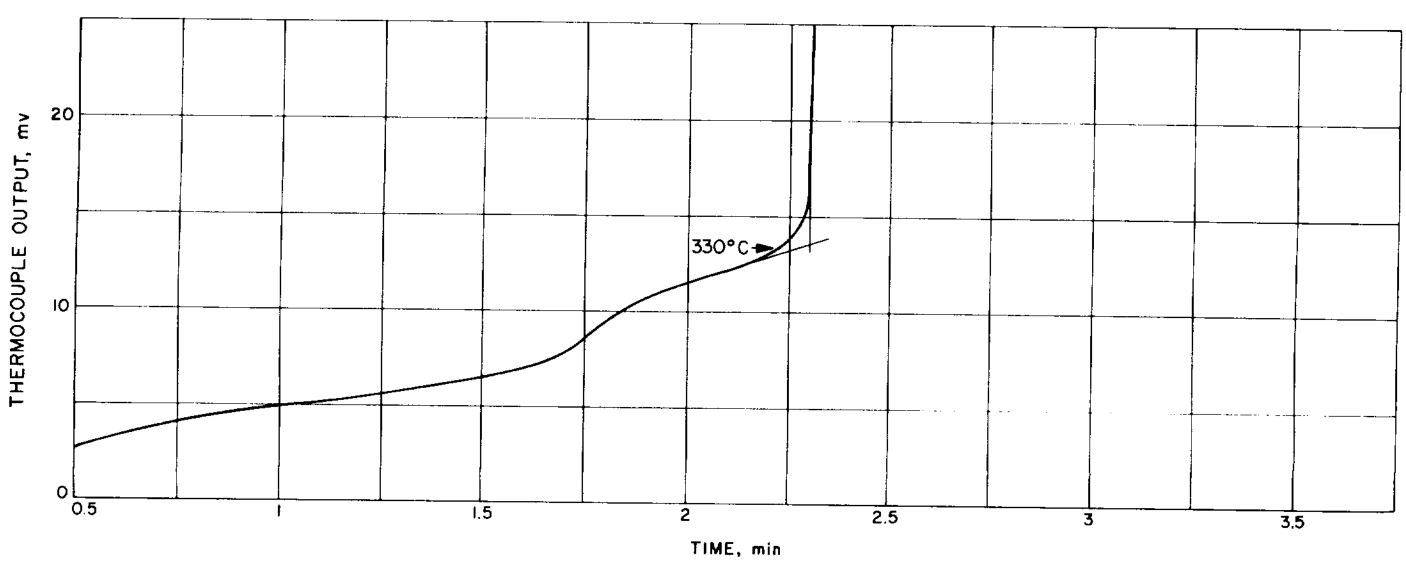

Fig. 8. <100μ lithium + carbon dioxide at 100 ml/min in tube reactor; ignition at 330°C

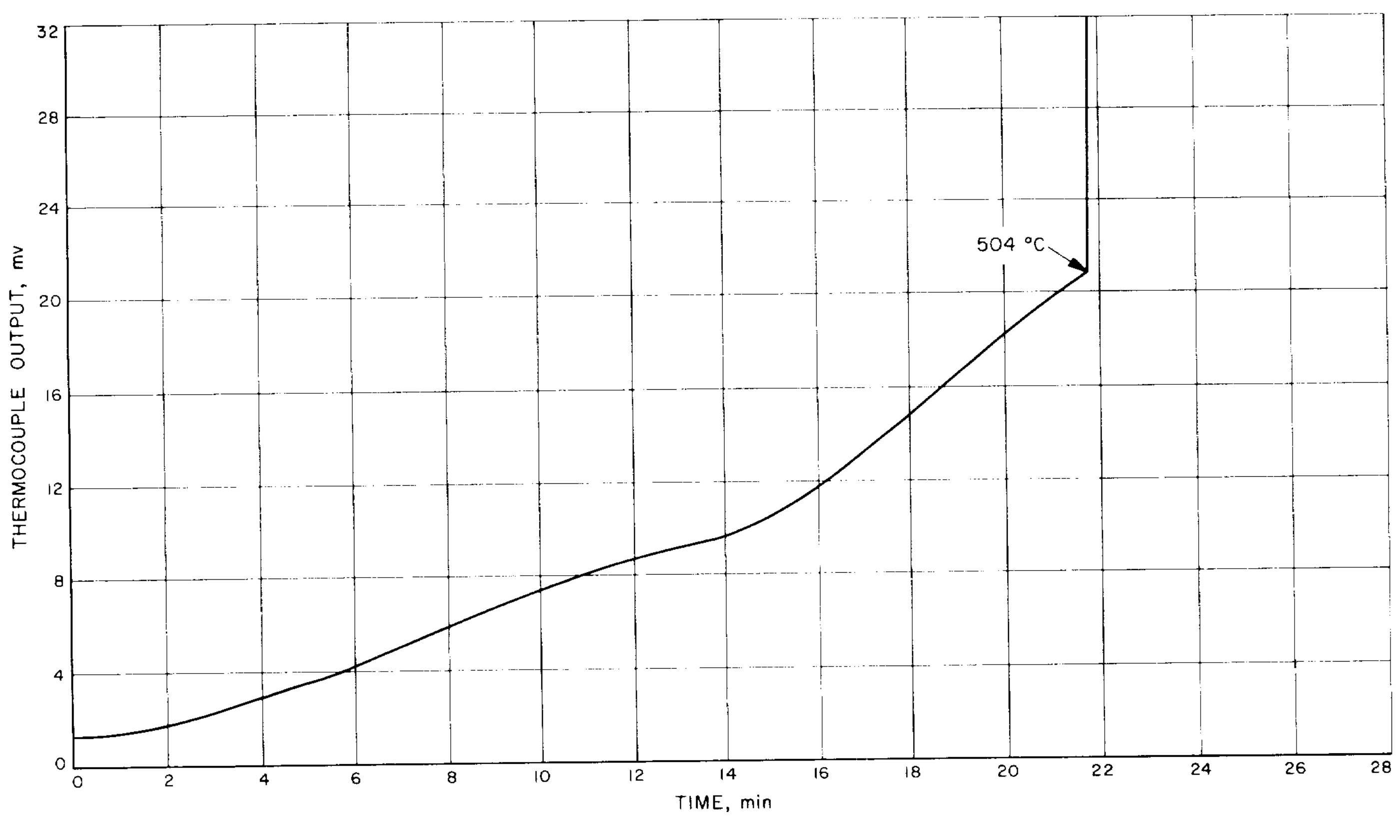

Fig. 9. 0.03μ beryllium + nitrogen in beryllium reaction tube; ignition at 504°C

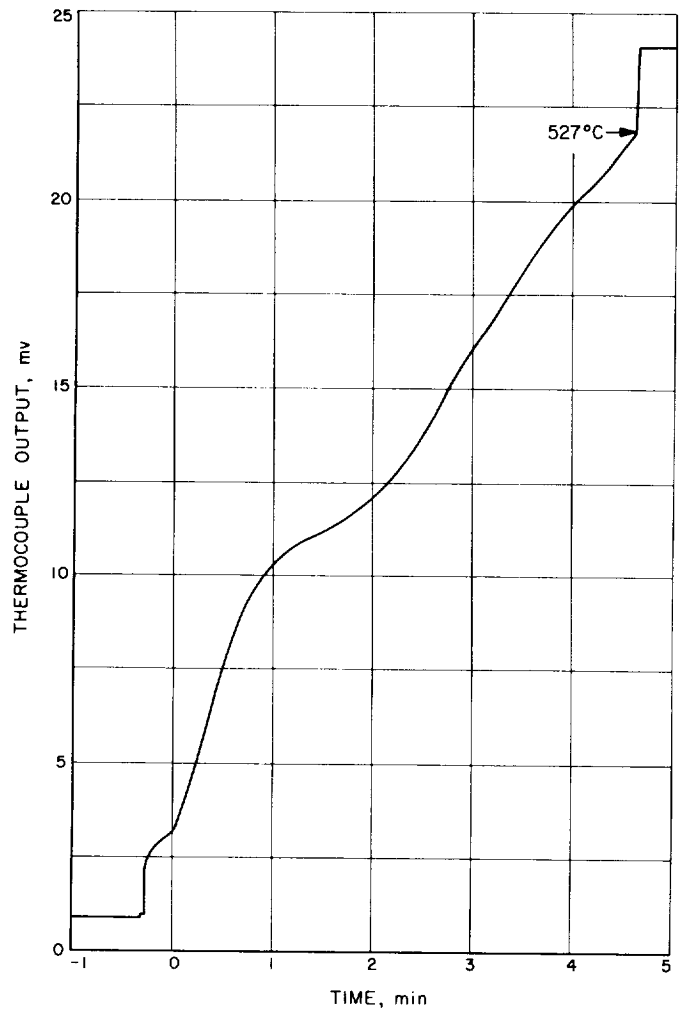

Fig. 10. 0.03μ beryllium + nitrogen in beryllium reaction tube; ignition at 527°C

Beryllium was reported to react at moderate speed with N_2 at 1100°C, although it reacts no more rapidly at 1300°C (Refs. 5, 6). Here, finely powdered Be (National Research Corp., Ultra Fine Beryllium Powder, $<0.1\mu$ particle size) was seen to ignite in air and in CO_2 at room temperature, and in the beryllium reaction tube at 504 and 527°C in N_2 (Figs. 9, 10).

Magnesium. The literature is somewhat contradictory regarding Mg in N_2. Mg powder (100%/100 mesh, 80%/270 mesh) ignited at 530°C (Refs. 7, 8) and also reacted readily when heated (Refs. 8, 9). Elsewhere it is reported that there is no reaction under 600°C (Ref. 10), and that the reaction begins at a temperature of 670°C (Ref. 11).

Here, Mg powder (Reade Manufacturing Co., Inc., −325 mesh, rated 99.9% pure) was heated to 954°C in N_2, and there was no indication of ignition (Fig. 11). There was a yellowish powder – presumably Mg_3N_2 – present after cooling, however. Some Mg powder was heated rapidly to 1071°C, and no ignition occurred in N_2 (Fig. 12). The yellow material was noted, however, after the tube cooled down. Heating Mg at 30 ml/min in CO_2 in the tube furnace, it was noted that ignition occurred at 749°C (Fig. 13). This compares to a literature value (Ref. 7) of 630°C for Mg powder.

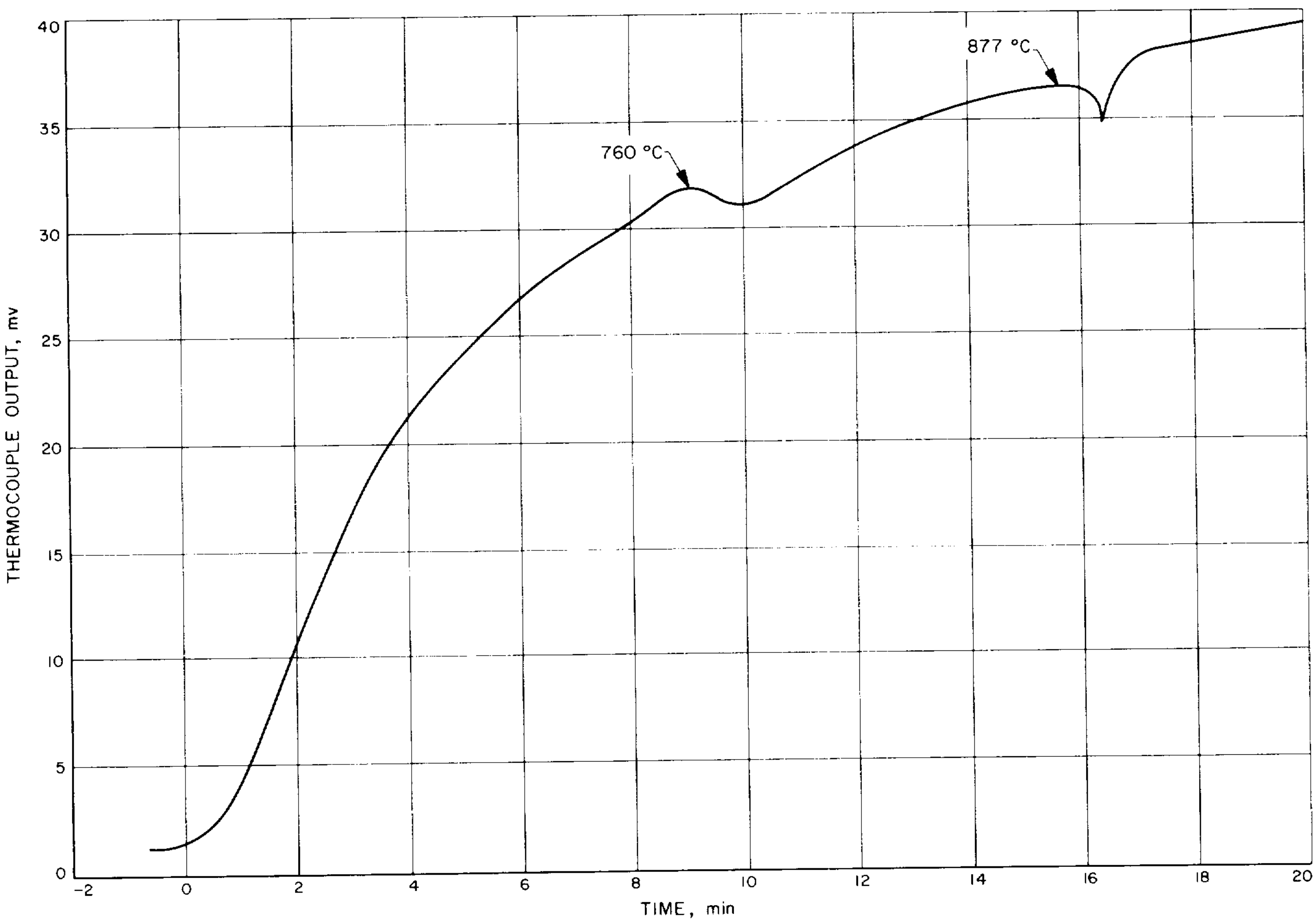

Fig. 11. −325 mesh magnesium + nitrogen in tube furnace apparatus; no evidence of ignition

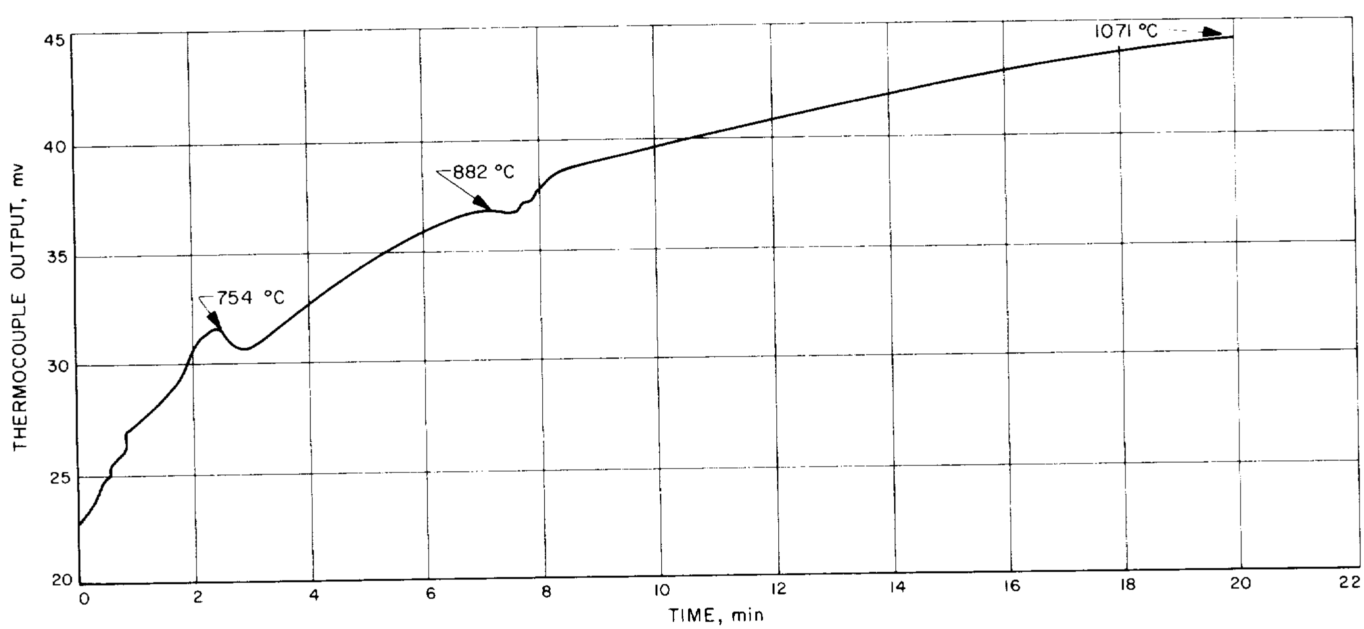

Fig. 12. −325 mesh magnesium + nitrogen in tube furnace apparatus; no evidence of ignition

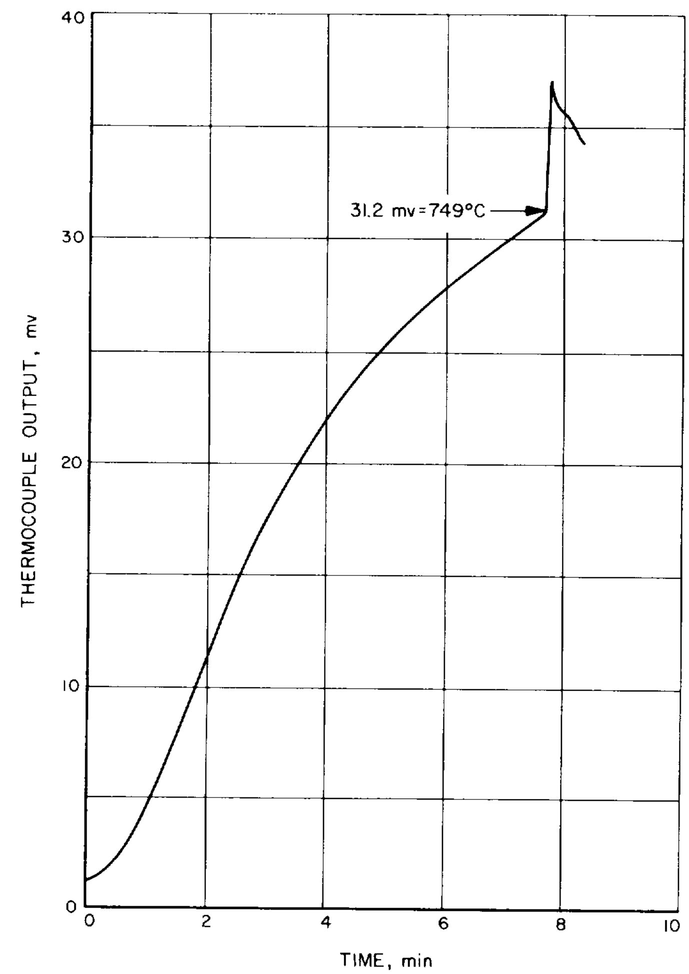

Fig. 13. −325 mesh magnesium + carbon dioxide at 30 ml/min in tube furnace apparatus; ignition at 749°C

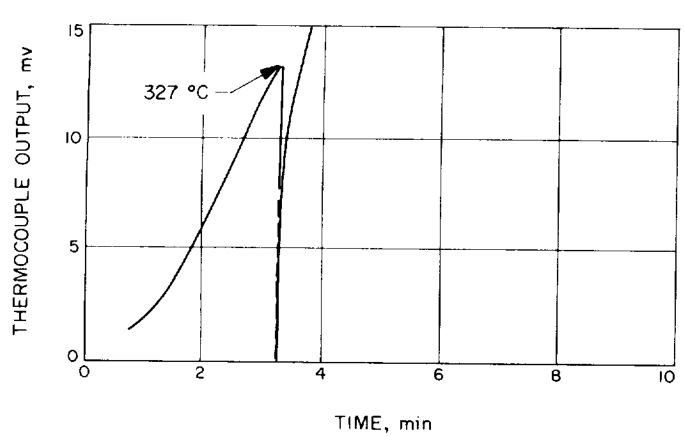

Fig. 14. −325 mesh calcium + nitrogen at 30 ml/min in tube furnace apparatus; ignition at 327°C

Calcium. Ignition of Ca in N_2 reportedly occurs at dull red heat (Refs. 12–15). Certain alloys of Ca can react faster or more slowly with N_2 (Ref. 16). Here, −325 mesh Ca powder (Research Chemicals Div. of Nuclear Corp. of America, 99.9% pure) was found in three experiments to ignite at 327 (Fig. 14), 360 (Fig. 15), and 671°C (Fig. 16) and observed to burn vigorously. After cooling and treating the solid product with water, an NH_3 odor

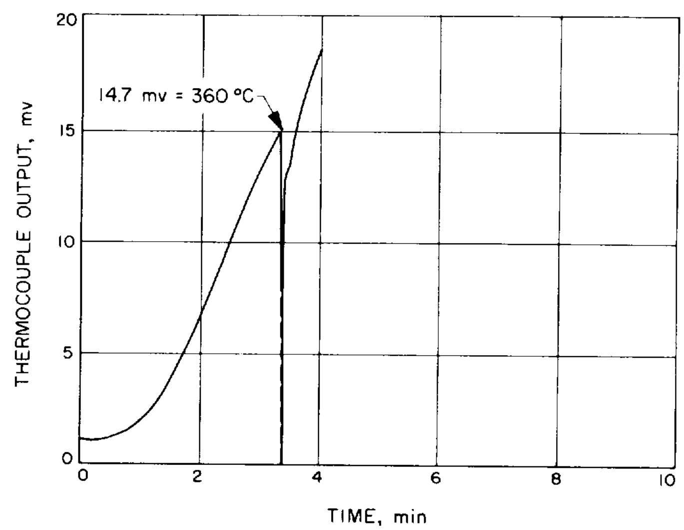

Fig. 15. −325 mesh calcium + nitrogen at 10 ml/min in tube furnace apparatus; ignition at 360°C

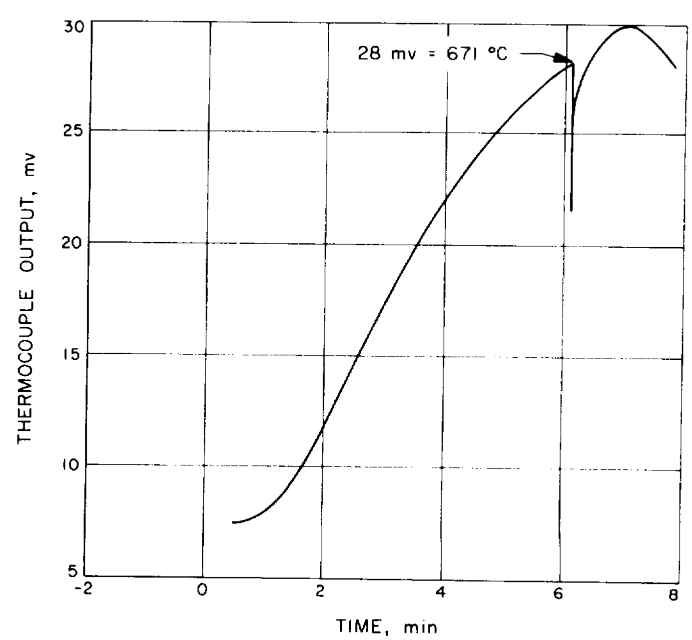

Fig. 16. −325 mesh calcium + nitrogen at 18.5 ml/min in tube furnace apparatus; ignition at 671°C

was observed, indicating the presence of Ca_3N_2 in the solid. The high ignition temperature in one case may be due to the formation of a protective nitride layer. It is of interest that ignition is indicated as an intense endotherm, and ignition and combustion were observed in the three cases. Ca also ignited in CO_2 at 293°C (Fig. 17) and burned quite brightly.

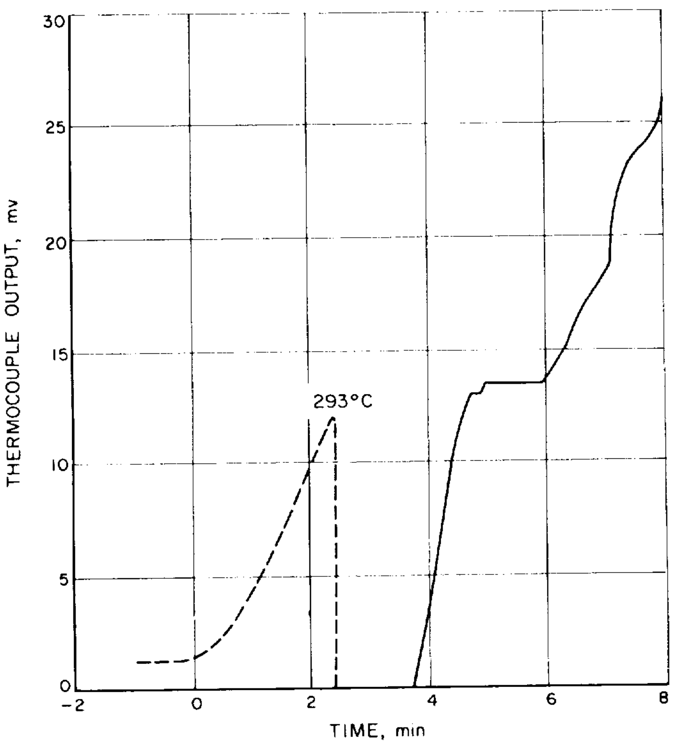

Fig. 17. −325 mesh calcium + carbon dioxide at 100 ml/min in tube furnace apparatus; ignition at 293°C

Boron. Amorphous B reportedly does not react with N_2 at 900°C, and the reaction begins at 1230°C (Refs. 17–20). Here, ultrafine B powder (National Research Corp., 0.02 to 0.06μ particle size) was heated in N_2 to 893°C in the tube reactor, and there was no evidence of ignition. A chemical analysis indicated 0.8% N in the product. Similarly, there was no indication of ignition of B in CO_2 heated to 920°C in the tube reactor.

Aluminum. In the literature, it was reported that powdered Al ignites at 720°C (Ref. 21) or 820°C (Refs. 22, 23). Others state that the reaction is vigorous but not self-sustaining at 700–750°C (Ref. 7), a reaction occurs above 800°C (Refs. 24, 25), and that the best temperature for AlN preparation is 900°C (Ref. 26). It was found here that neither powdered Al (Reynolds Aluminum 1-131 Atomized Powder, 99.3% pure, average particle size 8–9μ) nor ultrafine aluminum powder (National Research Corp., 93% pure, with oxide as the impurity, 0.03μ average particle size) ignited in N_2. The ultrafine powdered Al was heated to 1020°C in the tube reactor, and no ignition occurred; some evidence of reaction was found at 977°C (Fig. 18). Figure 19 shows some evidence of ignition at 1080°C.

Al powder (−325 mesh) reportedly ignited in CO_2 at 655°C (Ref 7). Here, the ultrafine powder ignited with CO_2 in the tube reactor at 360°C (Fig. 20) and 420°C (Fig. 21) and burned vigorously. However, when Al was

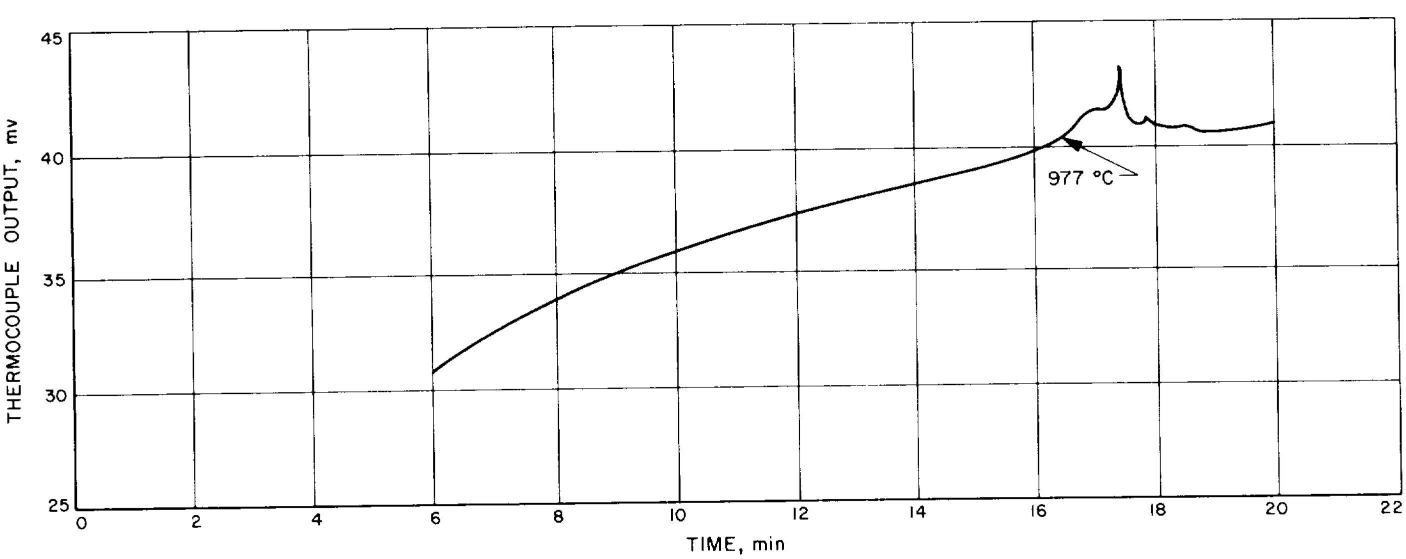

Fig. 18. 0.03μ aluminum + nitrogen at 100 ml/min in tube furnace apparatus; some evidence of ignition at 977°C

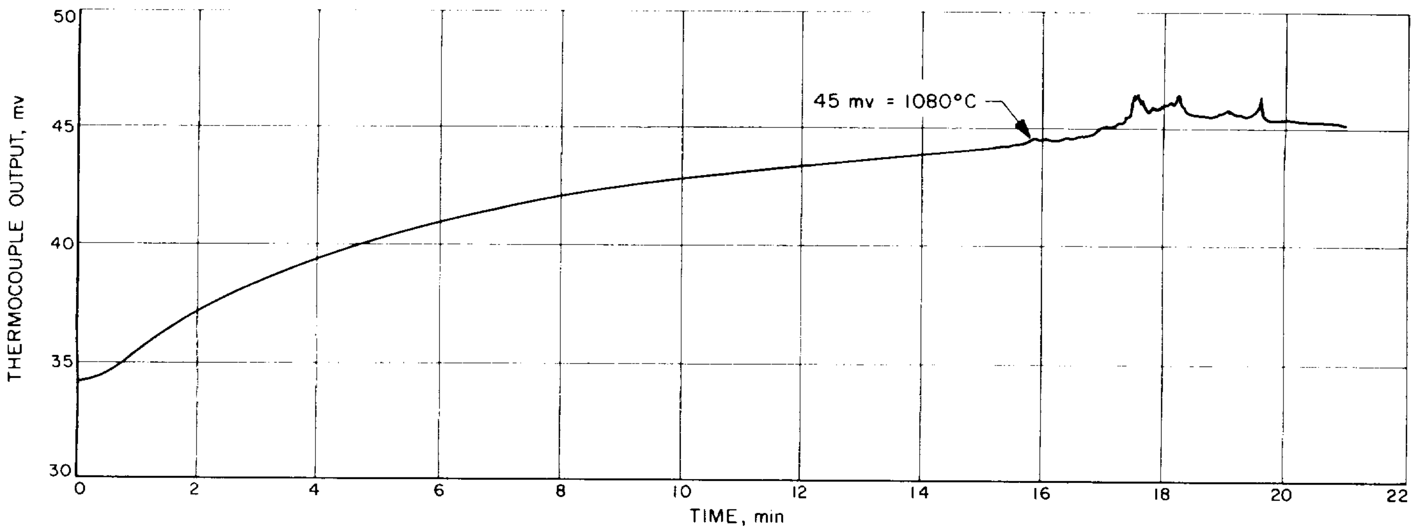

Fig. 19. 0.03μ aluminum + nitrogen at 100 ml/min in tube furnace apparatus; some evidence of ignition at 1080°C

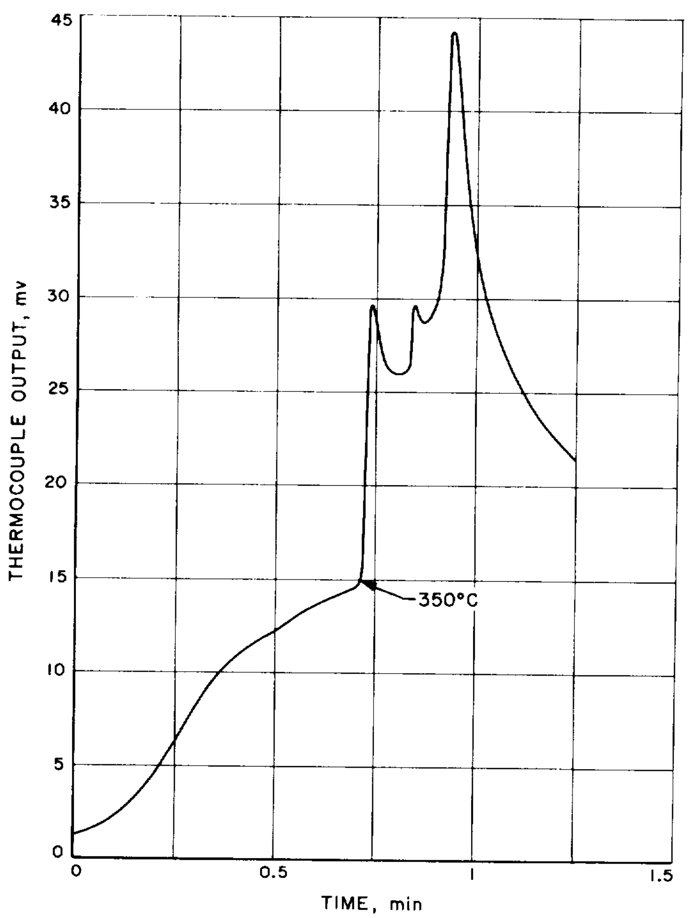

Fig. 20. 0.03μ aluminum + carbon dioxide at 100 ml/min in tube reactor; ignition at 360°C

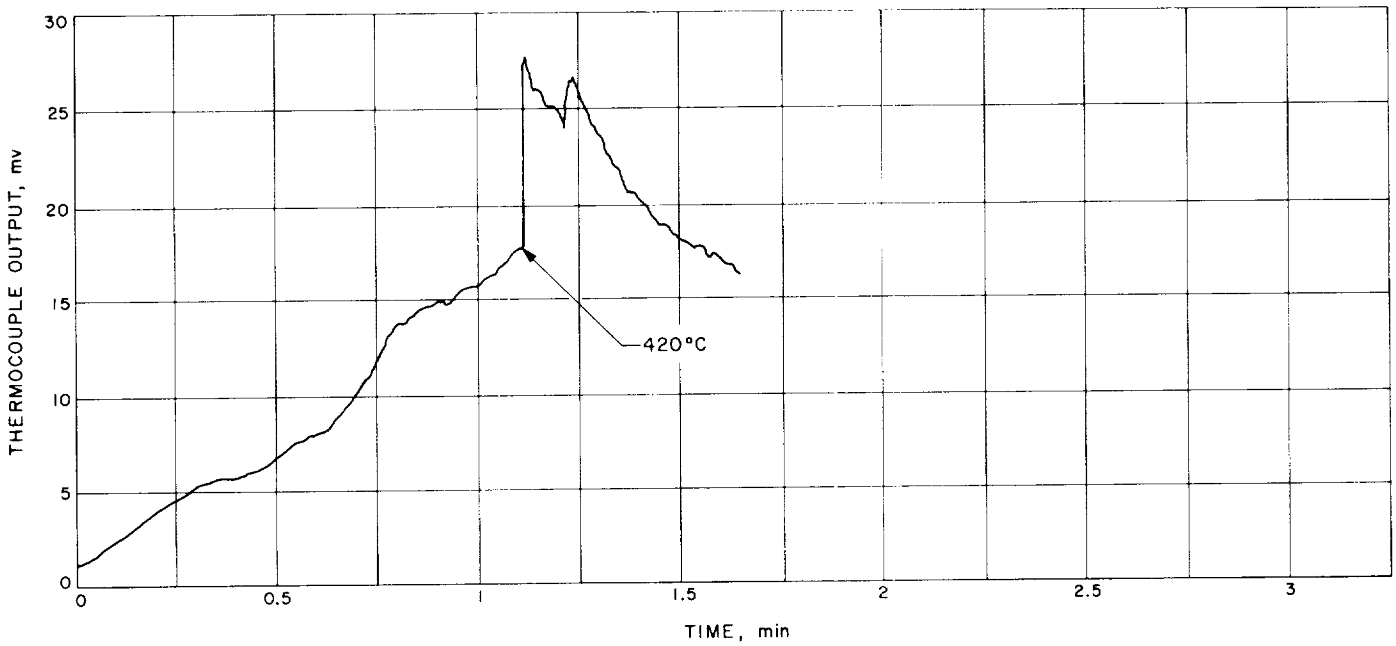

Fig. 21. 0.03μ aluminum + carbon dioxide at 100 ml/min in tube reactor; ignition at 420°C

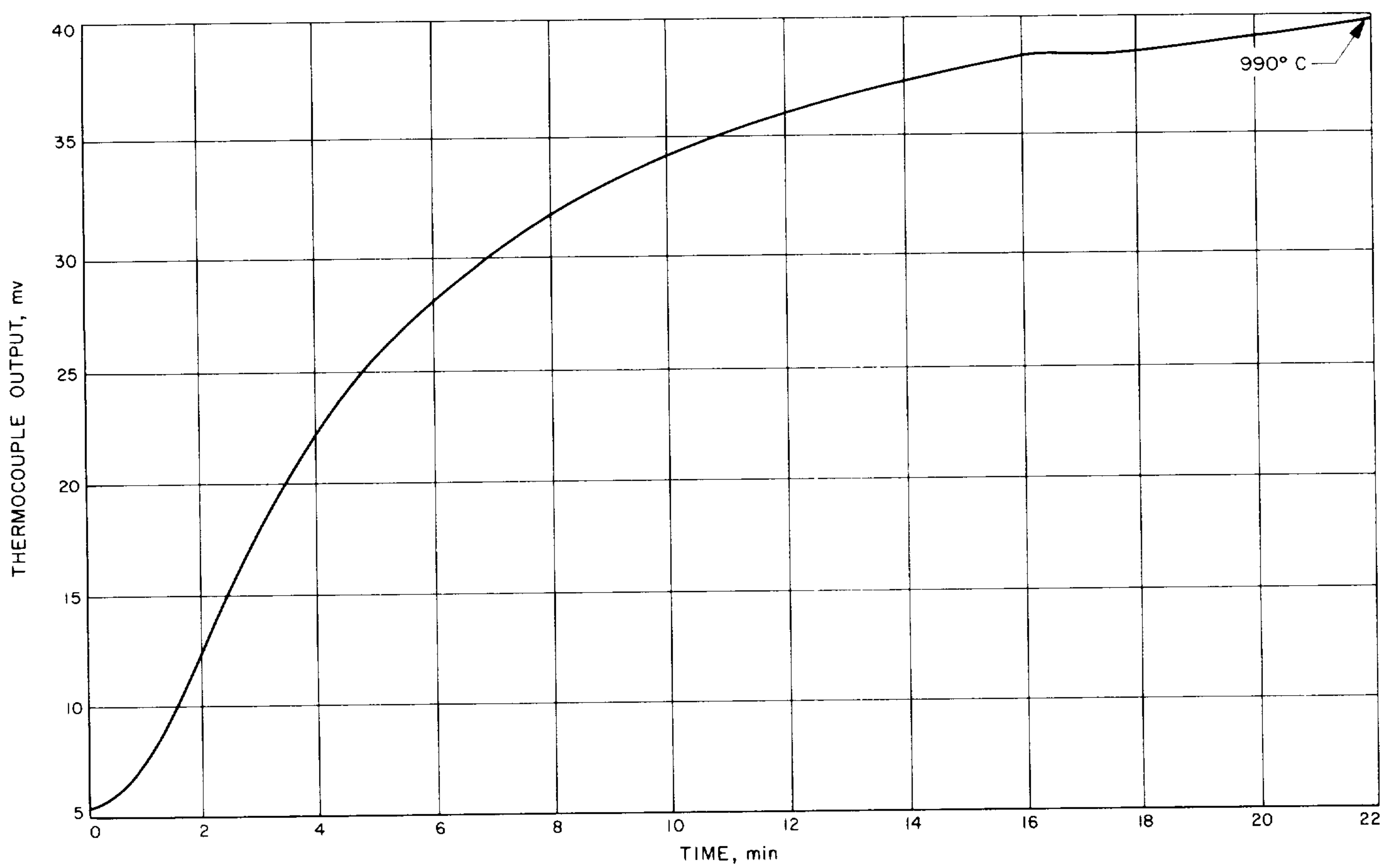

Fig. 22. 0.03μ aluminum + carbon dioxide at 100 ml/min in tube furnace apparatus; no evidence of ignition

heated with CO_2 in the tube furnace apparatus (Fig. 22), no ignition was observed, in spite of the fact that when the sample holder (Fig. 3) was removed and ultrafine Al powder sprinkled into the hot (980°C) tube furnace with CO_2 comi.g through at 100 ml/min, the powder ignited. Hence, the failure of the Al to ignite with CO_2 in the tube furnace is attributed to the fact that the Al had already oxidized below its ignition temperature.

Cerium. It is found in the literature that Ce ignited and burned in N_2 at 780°C (Ref. 27) and Ce wire ignited in N_2 at 850°C (Ref. 28). Here, Ce powder (VARLACOID Chemical Co., New York, order No. BH4-288601, −325 mesh, packed under kerosene), after having the kerosene removed by extraction with hexane, was seen to ignite at 216°C with N_2 in the tube furnace (Fig. 23) and at 230°C in the tube reactor (Fig. 24) to produce intense combustion. Treatment of the solid product with water after it had cooled down produced NH_3, indicating that the nitride was, indeed, formed.

When Ce was heated with CO_2 at 100 ml/min in the tube reactor, ignition and combustion were observed at 97°C (Fig. 25), 172°C (Fig. 26), and 190°C (Fig. 27). The low ignition temperature of 97°C is interesting; it is probably due to a hot spot caused by uneven heating of the tube reactor.

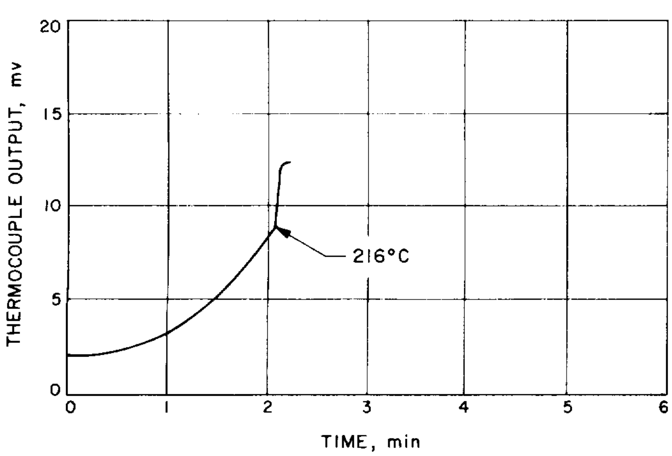

Fig. 23. −325 mesh cerium + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 216°C

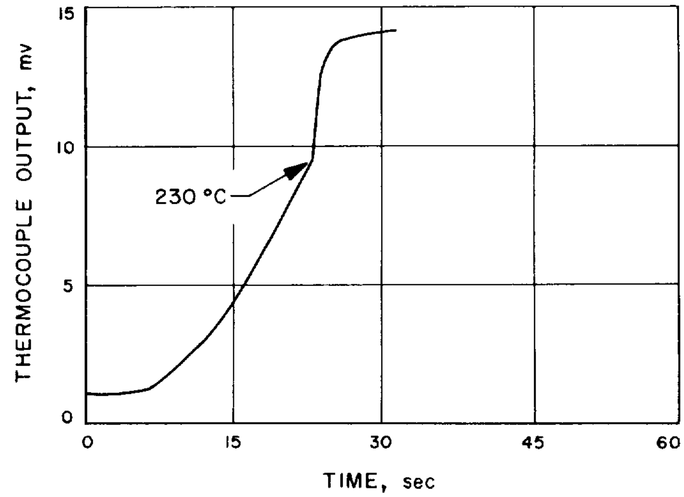

Fig. 24. −325 mesh cerium + nitrogen at 100 ml/min in tube reactor; ignition at 230°C

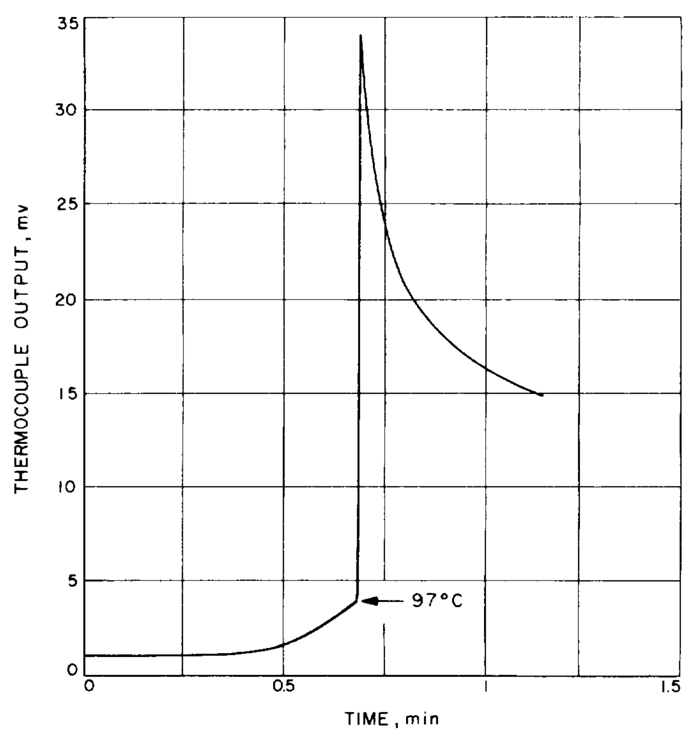

Fig. 25. −325 mesh cerium + carbon dioxide at 100 ml/min in tube reactor; ignition at 97°C

Mischmetall. Powdered Ce mischmetall (VARLACOID Chemical Co., New York, order No. BH4-288601; −325 mesh, packed under kerosene) was treated with hexane to remove the kerosene and was found to ignite in N_2 at 177°C in the tube reactor (Fig. 28) and at 209°C in the tube furnace (Fig. 29). It was found that a vigorous combustion occurred with mischmetall initiated at 160°C in CO_2 at 100 ml/min in the tube reactor (Fig. 30).

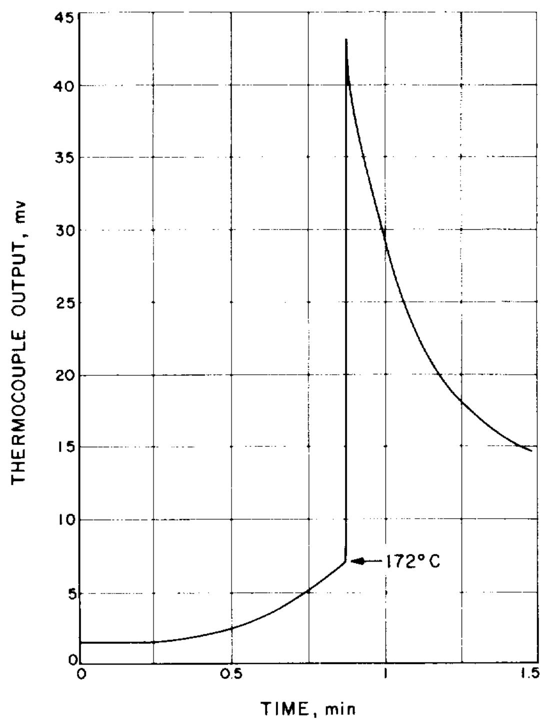

Fig. 26. −325 mesh cerium + carbon dioxide at 100 ml/min in tube reactor; ignition at 172°C

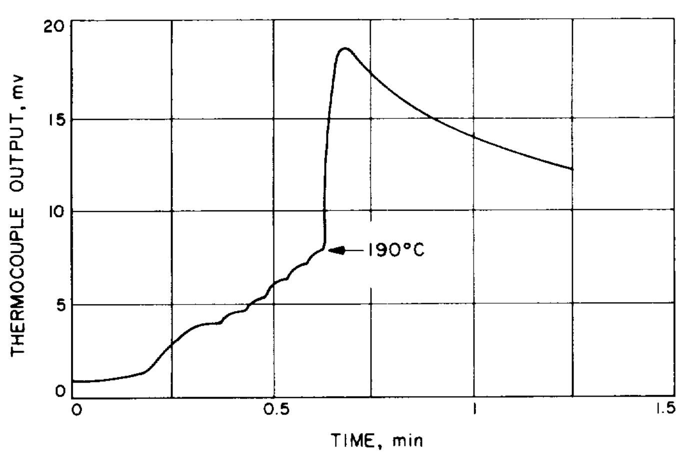

Fig. 27. −325 mesh cerium + carbon dioxide at 100 ml/min in tube reactor; ignition at 190°C

Titanium. According to the literature, molten Ti burned in N_2 (Ref. 29), highly divided Ti burst into flame in N_2 at 800°C (Refs. 30, 31), and 10.5μ Ti powder ignited in commercial N_2 at 760°C (Ref. 30). Here, powdered Ti (A. D. Mackay Co., New York, 1–5μ particle size) ignited in N_2 at 850°C in the tube furnace apparatus (Fig. 31). It is noted that the initial N_2 temperature was 540°C. It was found necessary to preheat the N_2 because the Ti did not ignite if the N_2 was initially at

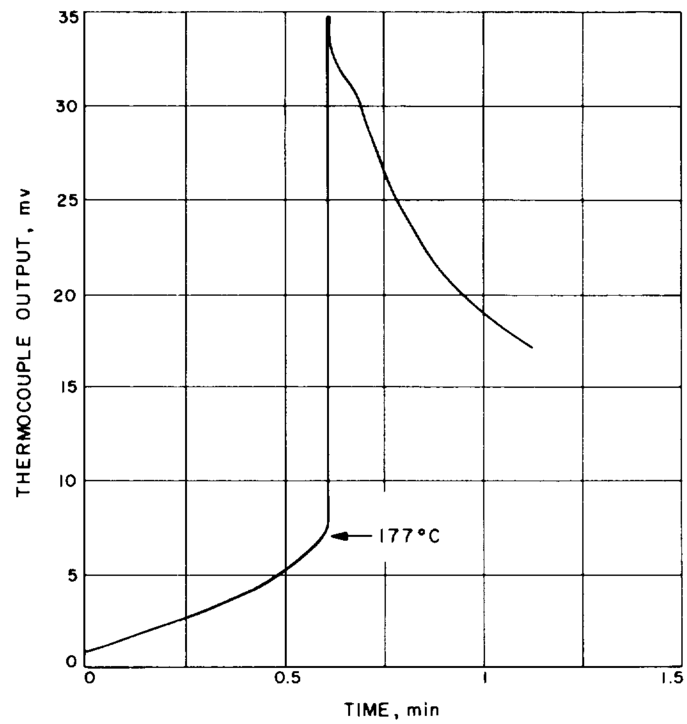

Fig. 28. −325 mesh mischmetall + nitrogen at 100 ml/min in tube reactor; ignition at 177°C

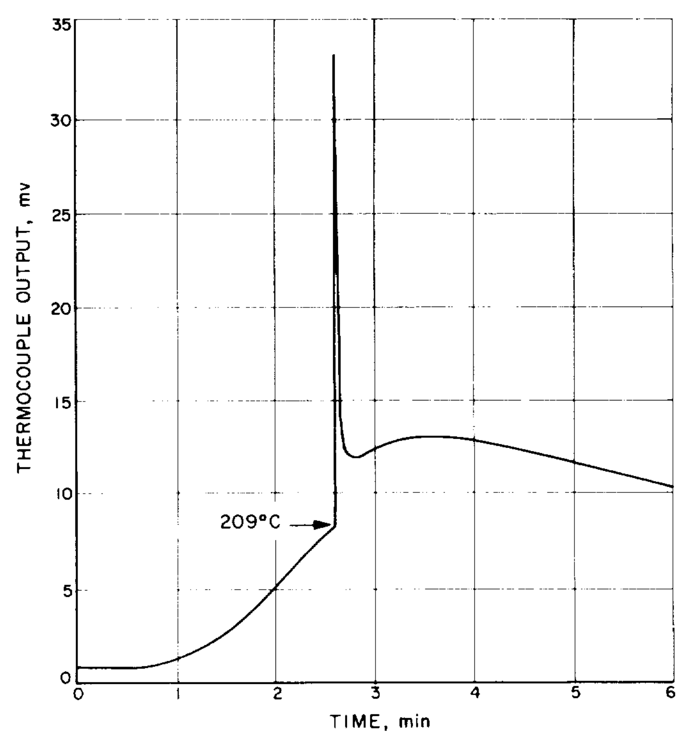

Fig. 29. −325 mesh mischmetall + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 209°C

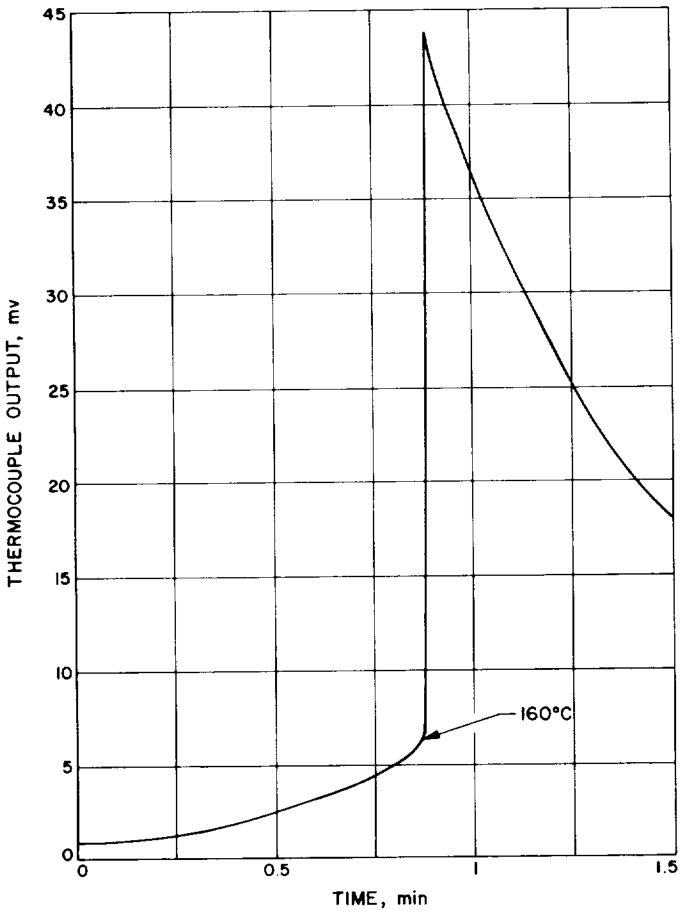

Fig. 30. −325 mesh mischmetall + carbon dioxide at 100 ml/min in tube reactor; ignition at 160°C

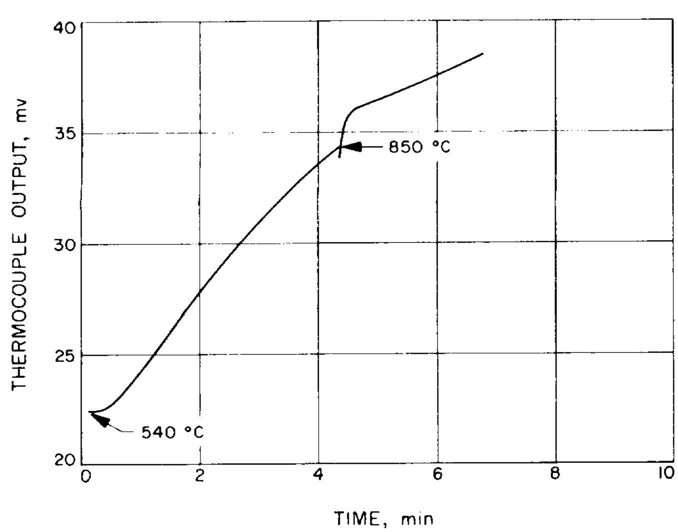

Fig. 31. 1–5μ titanium + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 850°C

ambient temperature. In conjunction with this, if the furnace was heated to 840°C, the tube and sample holder evacuated, the crucible full of powdered Ti lowered into the furnace, and the N_2 then added to the system, ignition occurred at once.

It is reported in the literature (Ref. 7) that powdered Ti ignited in CO_2 at 680°C. Here, in an initial experiment, the Ti ignited at red heat in CO_2, and in a subsequent experiment, using CO_2 at 100 ml/min in the tube furnace, it was seen that ignition occurred at 670°C (Fig. 32).

Zirconium. The ignition temperature for powdered Zr in N_2 is reported in the literature as 530°C for −325 mesh (Ref. 7), 790°C for 3.3μ particles (Ref. 30), and no ignition at 820°C for 17.9μ particles (Ref. 30).

Here, for 3μ Zr powder (Charles Hardy, Inc., zirconium powder 120-A grade, lot 103-2, order No. BH4-288629, 94–95% pure, oxide impurity) no ignition was

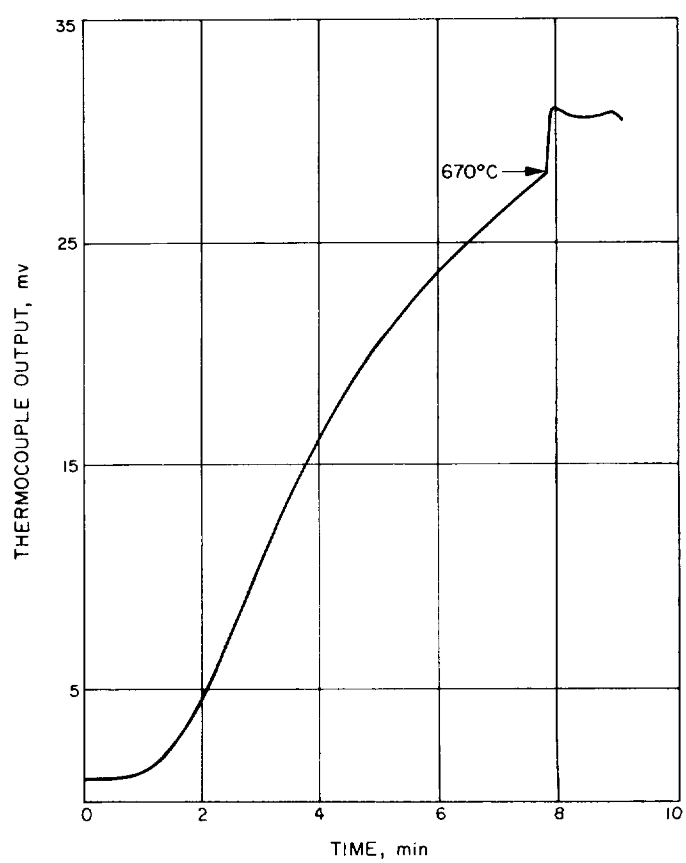

Fig. 32. 1–5μ titanium + carbon dioxide at 100 ml/min in tube furnace apparatus; ignition at 670°C

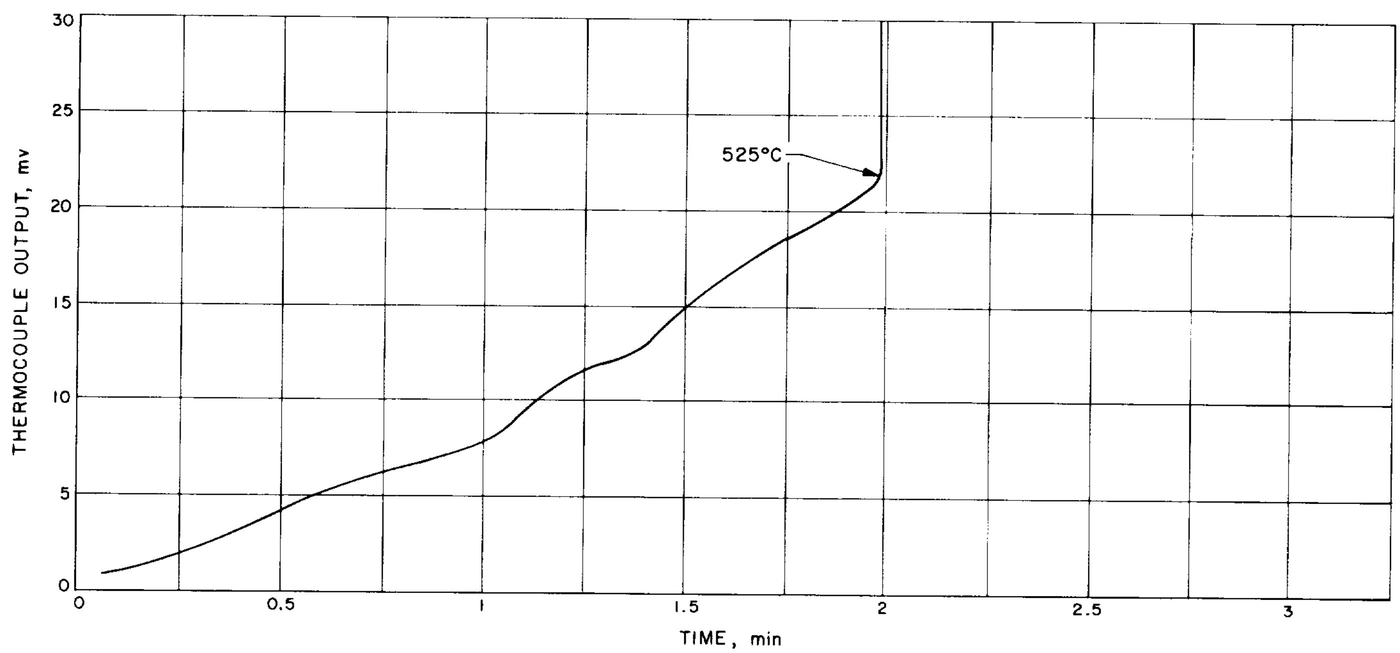

Fig. 33. 3μ zirconium + nitrogen at 100 ml/min in tube reactor; ignition at 525°C

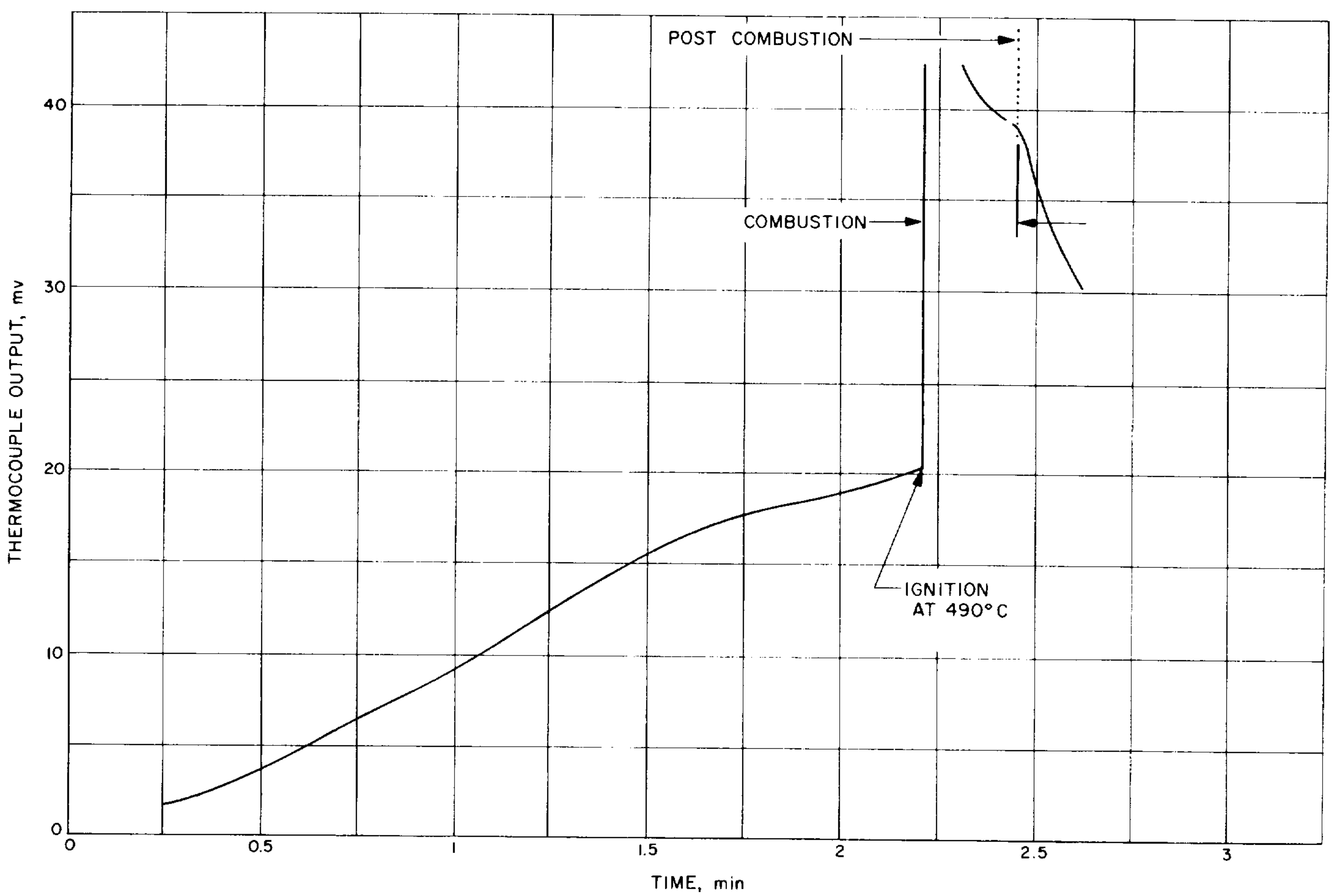

Fig. 34. 3μ zirconium + nitrogen at 100 ml/min in tube reactor; ignition at 490°C

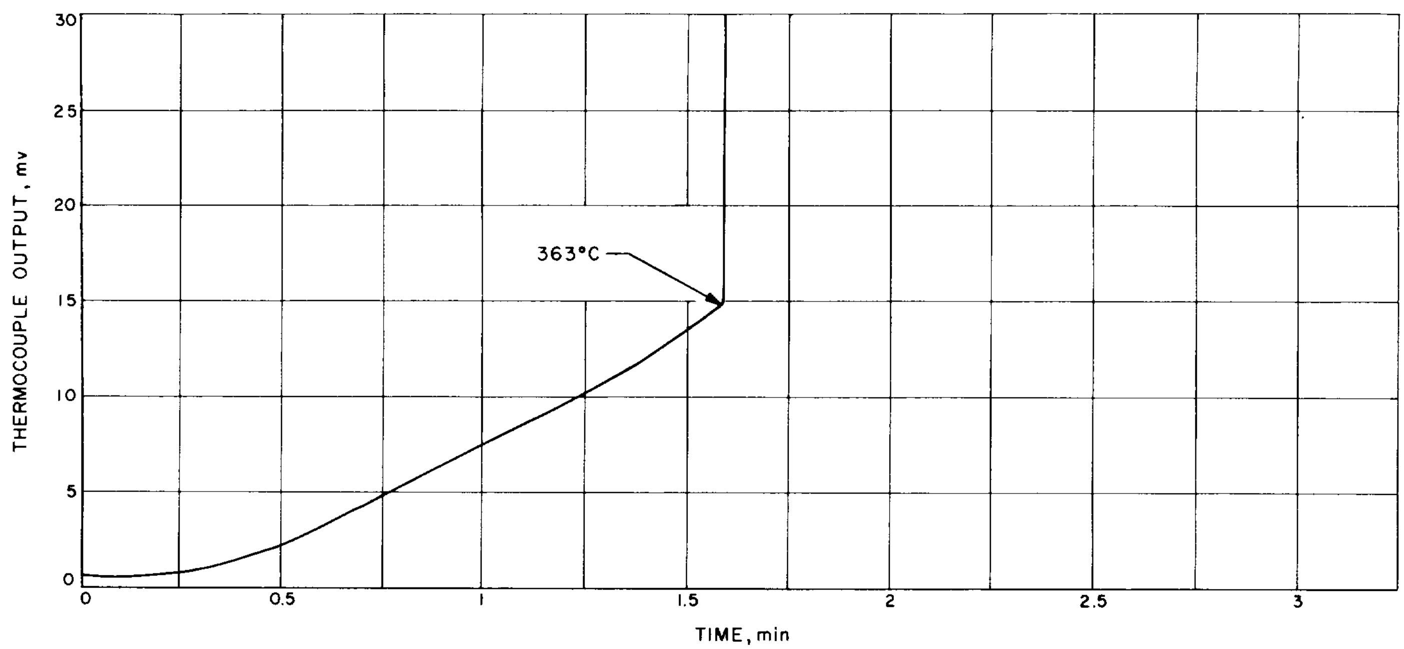

Fig. 35. 3μ zirconium + carbon dioxide at 100 ml/min in tube reactor; ignition at 363°C

observed in the tube furnace apparatus on heating from 25 to 970°C, but in the tube reactor vigorous ignition was seen at 525 and 490°C in two experiments (Figs. 33, 34). For the reaction of CO_2 and Zr, the reported ignition temperature for Zr powder is 560°C. Two experiments conducted here in the tube reactor using a CO_2 rate of 100 ml/min show ignition temperatures of 363 (Fig. 35) and 366°C (Fig. 36).

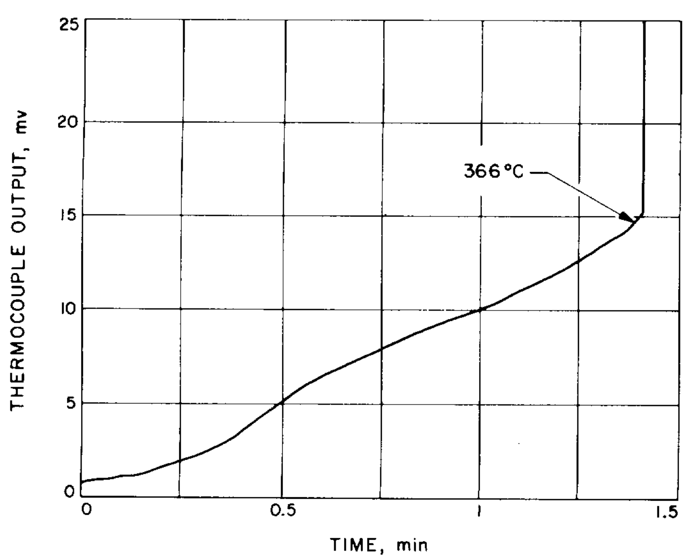

Fig. 36. 3μ zirconium + carbon dioxide at 100 ml/min in tube reactor; ignition at 366°C

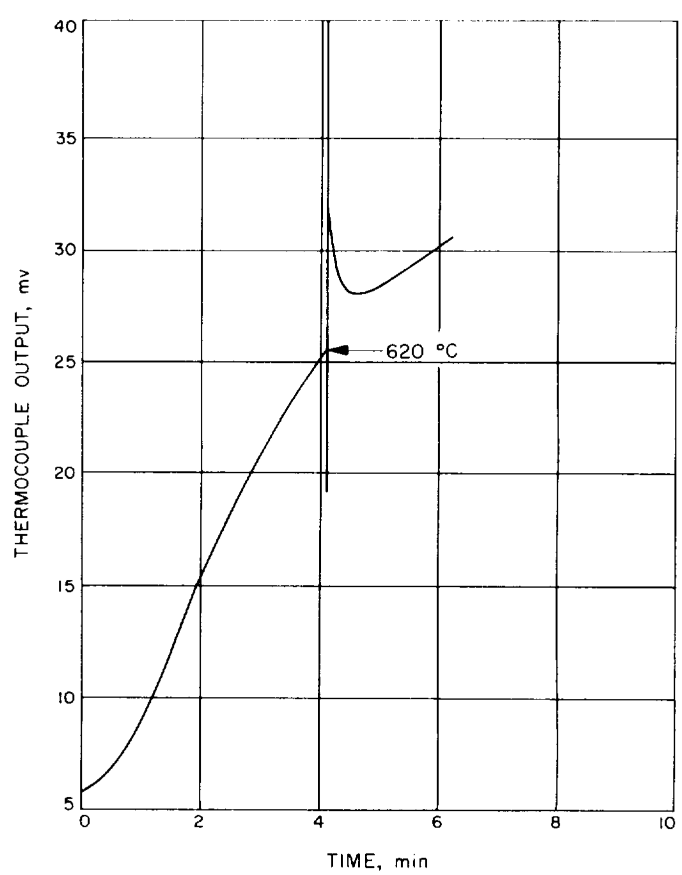

Fig. 37. −325 mesh thorium + nitrogen at 60 ml/min in tube furnace apparatus; ignition at 620°C

Thorium. Reportedly, 7.2μ Th powder ignited at 500°C in commercial N_2 and at 450°C in CO_2 (Ref. 31). Here, −325 mesh Th powder (Charles Hardy, Inc., order No. BH4-288629) was seen to ignite at 830 and 620°C in N_2 at 60 ml/min in the tube furnace (Figs. 37, 38); it ignited at 730°C in CO_2 at 200 ml/min in the tube reactor (Fig. 39).

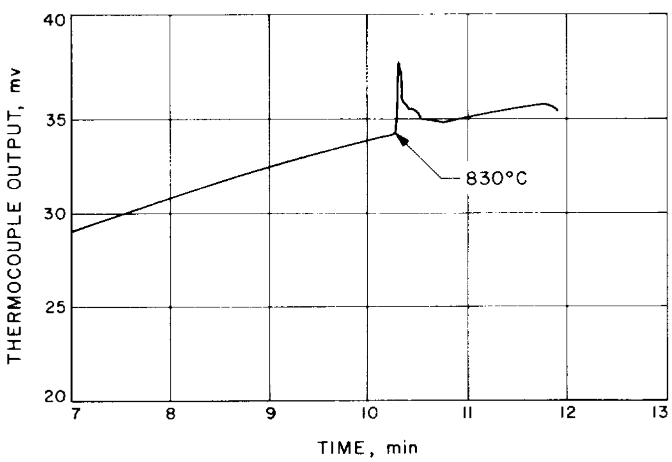

Fig. 38. −325 mesh thorium + nitrogen at 60 ml/min in tube furnace apparatus; ignition at 830°C

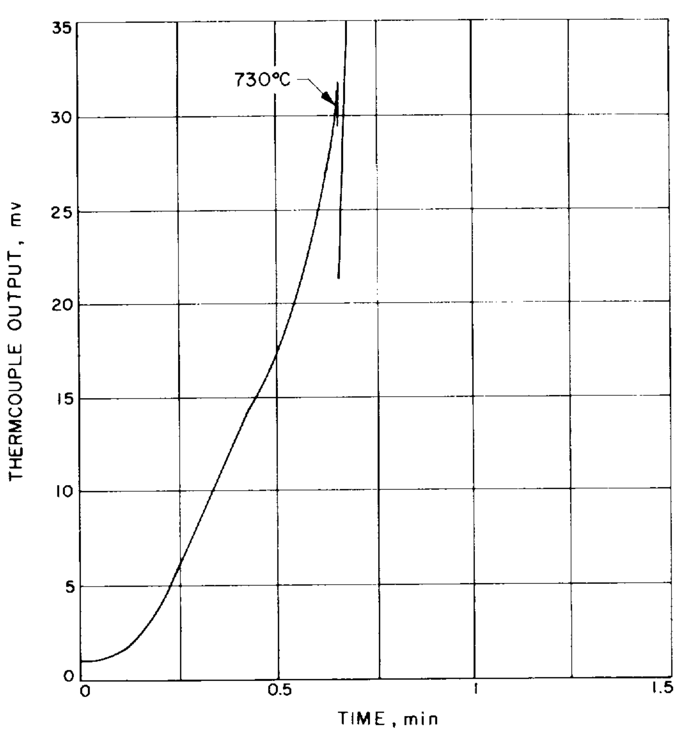

Fig. 39. −325 mesh thorium + carbon dioxide at 200 ml/min in tube reactor; ignition at 730°C

Uranium. From the literature, it is found that 10.8μ U^{238} powder ignited in commercial N_2 at 410 and in CO_2 at 350°C (Ref. 30). Here, −200 mesh U^{238} (The Great Southern Manufacturing and Sales Co., depleted uranium, coated with 2% Viton) was found to ignite in N_2 in two experiments at 354°C in the tube reactor (Fig. 40) and at 360°C in the tube furnace apparatus (Fig. 41), each using a 100 ml/min flow rate. In the tube reactor, with CO_2 at 100 ml/min, U^{238} ignited at 235°C (Fig. 42).

Chromium. Although it was reported by some authors that pyrophoric Cr, prepared by distilling its amalgam, ignited in N_2 when warmed (Refs. 29, 32), others report a slow reaction on heating (Refs. 15, 17, 33). Here, −325 mesh Cr powder, 99.85% pure (VARLACOID Chemical Co., New York, order No. BH4-288601), was heated to 1170°C in the tube reactor (Fig. 43), and there was no evidence of ignition. On heating in CO_2 at 100 ml/min in the tube reactor, the mass suddenly glowed at 870°C (Fig. 44), indicating a type of ignition.

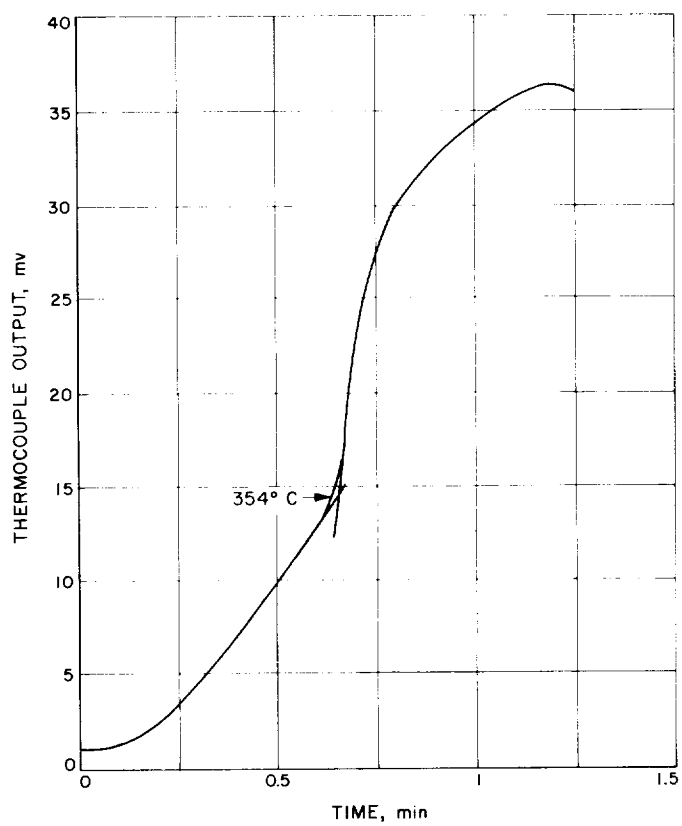

Fig. 40. −200 mesh uranium + nitrogen at 100 ml/min in tube reactor; ignition at 354°C

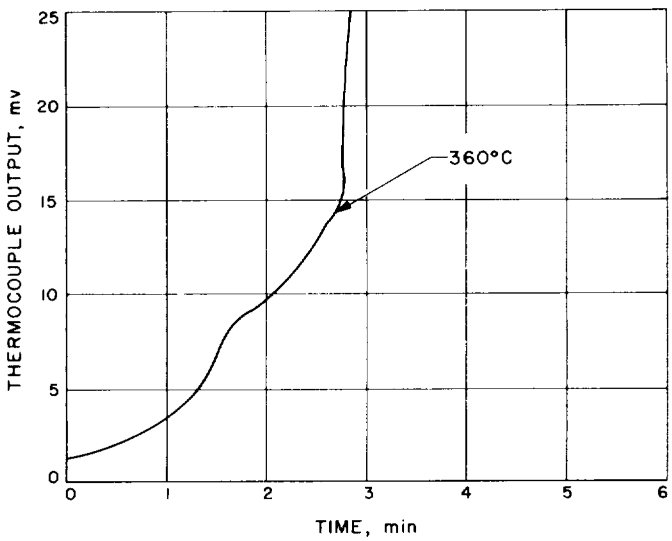

Fig. 41. −200 mesh uranium + nitrogen at 100 ml/min in tube furnace apparatus; ignition at 360°C

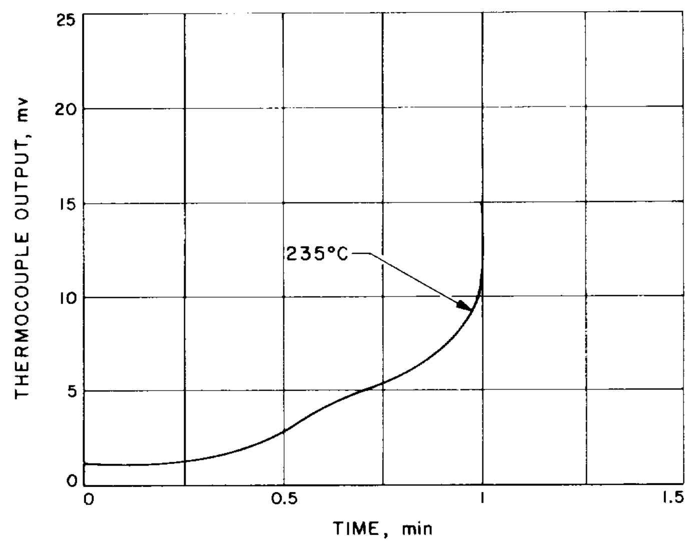

Fig. 42. −200 mesh uranium + carbon dioxide at 100 ml/min in tube reactor; ignition at 235°C

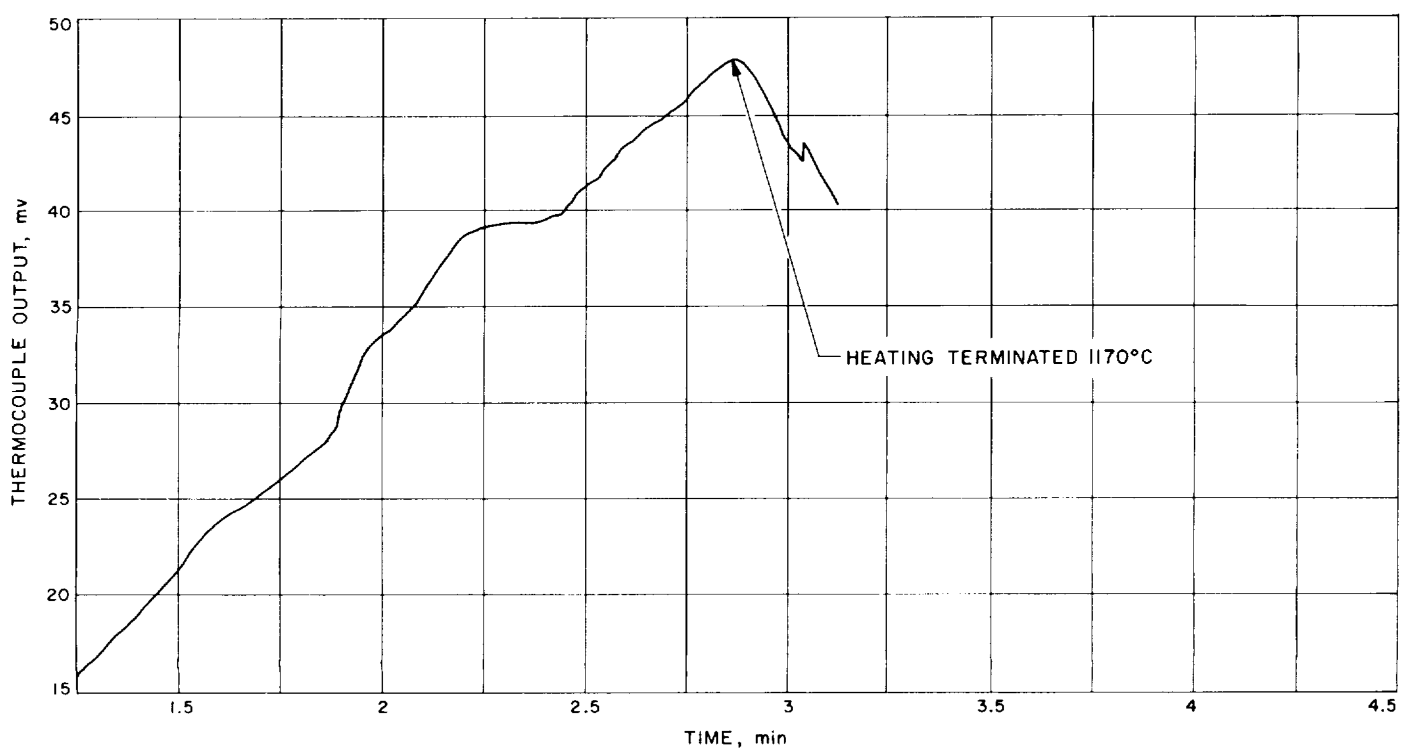

Fig. 43. −325 mesh chromium + nitrogen at 100 ml/min in tube reactor; no evidence of ignition

Manganese. Although it was reported that finely divided Mn reacted with N_2 when heated (Refs. 15, 29, 33, 34), there was no mention of ignition. Here, −325 mesh Mn powder, 99% pure (Charles Hardy, Inc., order No. BH4-288629) was heated to 1316°C in the tube reactor, and there was no indication of ignition. However, when the MN was heated with CO_2 at 100 ml/min in the tube reactor, the mass began to glow at 696°C (Fig. 45) and appeared to burn, but the combustion was not vigorous.

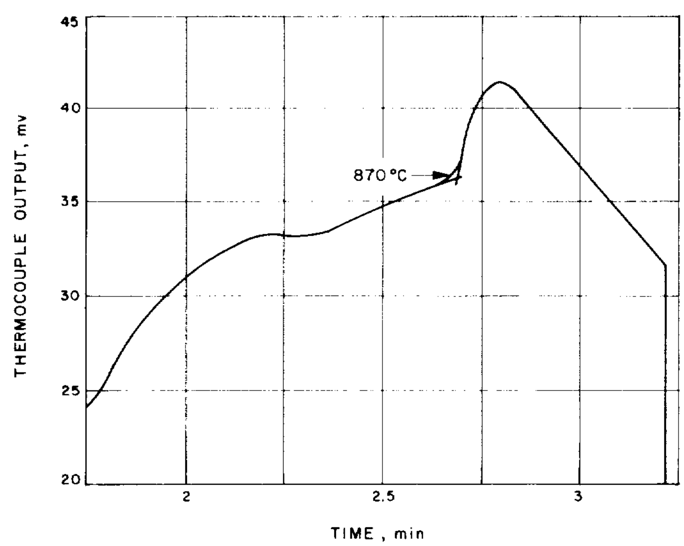

Fig. 44. −325 mesh chromium + carbon dioxide at 100 ml/min in tube reactor; ignition at 870°C

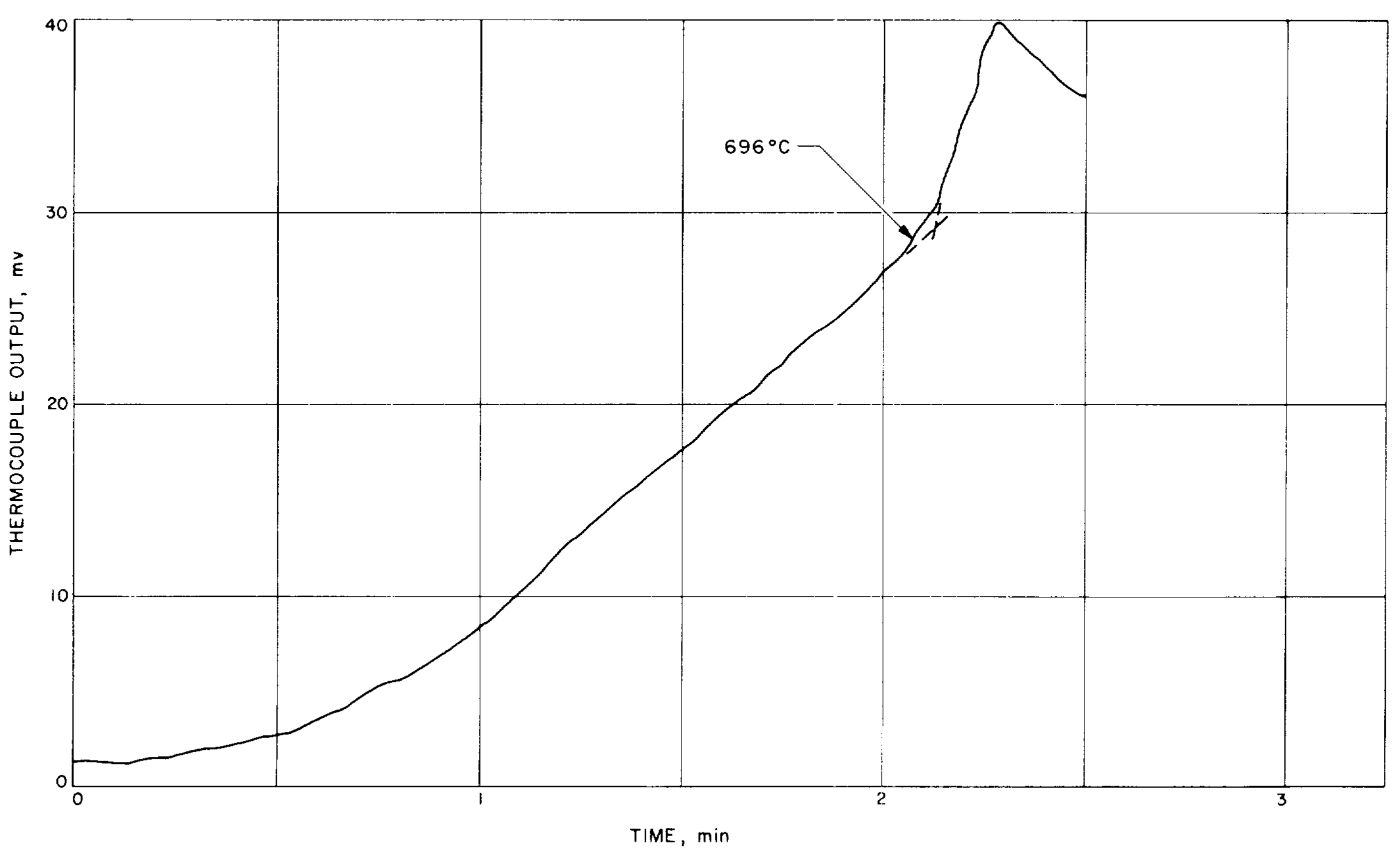

Fig. 45. −325 mesh magnesium + carbon dioxide at 100 ml/min in tube reactor; ignition at 696°C

IV. SUMMARY AND DISCUSSION

The results summarized in Table 1 indicate that there are several fuels that could be used in the atmosphere of Mars or Venus, the most promising being ultrafine powdered beryllium; lithium, however, is another promising material, and aluminum and magnesium have potential. The high toxicity of beryllium and the considerable corrosiveness of lithium present problems which must be dealt with in developing a propulsive device which uses Li or Be as fuel.

An extension of this program might take the following direction: the ignition temperature of the fuel would be found in the simulated planetary atmosphere and the heat of combustion and the combustion products determined. Then, a prototype burner would be developed and work done to optimize its performance. Finally, the burner would be incorporated in some type of engine, such as a ramjet or gas turbine, which would provide propulsion.

Table 1. Summary of results

Metal	Condition	Ignition Temperature[a], °C	
		in N_2	in CO_2
Lithium	<100μ	388, 410	330[b]
Beryllium	<0.1μ	504[c], 527[c]	25[c]
Magnesium	−325 mesh	No ignition to 1071[b]	749[b]
Calcium	−325 mesh	327, 360, 671	293[b]
Boron	0.02–0.06μ	No ignition to 893[b]	No ignition to 920[b]
Aluminum	8–9μ 0.03μ	No ignition to 1080	360[b], 420[b]
Cerium	−325 mesh	216, 230[b]	97, 172, 190[b]
Mischmetall	−325 mesh	209, 177[b]	160[b]
Titanium	1–5μ	830	670[b]
Zirconium	3μ	490, 525[b]	363, 366[b]
Thorium	−325 mesh	620	730[b]
Uranium	−200 mesh, Viton-coated	354[b], 360	235[b]
Chromium	−325 mesh	No ignition to 1170[b]	870[b]
Manganese	−325 mesh	No ignition to 1316[b]	696[b]

[a] In tube furnace unless otherwise specified.
[b] In tube reactor.
[c] In beryllium reaction tube.

REFERENCES

1. Markowitz, M. M., and Boryta, D. A., "Lithium Metal-Gas Reactions," *Journal of Chemical and Engineering Data*, Vol. 7, Oct. 1962, pp. 586–591.

2. Dafert, F. W., and Miklauz, R., "New Compounds of Nitrogen and Hydrogen With Lithium," *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*, Vol. 31, 1910, pp. 981–996.

3. Norton, T. H., *Consular Report on the Utilization of Atmospheric Nitrogen*, Washington, 1912, p. 138.

4. Ouvrard, L., "On a Nitride of Lithium," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 114, 1892, p. 120.

5. Fichter, F., and Brunner, E., "Beryllium Nitride," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 93, 1915, p. 84.

6. von Antropoff, A., and Kruger, K. H., "Kinetics of the Reaction of the Alkaline Earth Metals With Nitrogen and Other Gases. II, III, IV," *Zeitschrift für physikalische Chemie*, Vol. A167, 1933, pp. 49–70.

7. Hartmann, I., Nagy, J., and Brown, H. R., "Inflammability and Explosibility of Metal Powders," *Report on Investigations*, U. S. Bureau of Mines, No. 3722, 1943.

8. Weintraub, A. A., "Flaming Metal," *Safety Engineering*, Vol. 99, No. 3, 1950, pp. 34–35, 47–48.

9. Merz, V., "Remarks on Magnesium," *Berichte der deutschen chemischen Gesellschaft*, Vol. 24, p. 3940.

10. Remy-Gennete, P., "Researches on the Alkaline Earth Hydrides," *Annales de Chimie*, Vol. 19, 1933, pp. 263–426.

11. Matignon, C., and Lassieur, "Action of Nitrogen and Oxygen on Magnesium," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 154, 1912, pp. 63–65.

12. Moissan, H., "Preparation and Properties of Calcium Nitride," *Bulletin de la Société Chimique de France*, Series 3, Vol. 21, 1899, p. 881.

13. Moissan, H., "Preparation and Properties of Calcium Nitride," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 127, 1898, p. 498.

14. Maquenne, L., "On the Fixation of Nitrogen by the Alkaline-Earth Metals," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 121, 1895, p. 1147.

15. Tammaun, G., "Velocity of Formation of Some Nitrides," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 124, 1922, pp. 25–35.

16. Ruff, O., and Lauterbach, H., "The Absorption of Nitrogen by Calcium and Its Alloys," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 121, 1922, p. 167.

17. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., Ltd., London, 1953, pp. 75–144.

REFERENCES (Cont'd)

18. Moissan, H., "Studies of the Properties of Amorphous Boron," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 114, 1892, p. 617.

19. Moissan, H., "Studies of Amorphous Boron," *Annales de Chimie et de Physique*, Series 7, Vol. 6, 1895, pp. 296, 313.

20. Rizzo, H. F., "Oxidation of Boron at Temperatures Between 400° and 1300° in Air," *Boron, Synthesis, Structure, and Properties*, Plenum Press, Inc., New York, N. Y., 1960, pp. 175–189.

21. Fichter, F., "Aluminum Nitride," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 54, 1907, p. 322.

22. Neumann, B., Kroger, C., and Haebler, H., "The Heat of Formation of Nitrides. II. The Heat of Nitriding of Lithium, Aluminum, Beryllium, and Magnesium," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 204, 1932, pp. 81–96.

23. Wolf, J., "Synthesis of Aluminum Nitride From the Elements," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 83, 1913, pp. 159–162.

24. Russ, F., "An Experiment Demonstrating the Formation of Aluminum Nitride," *Zeitschrift für Elektrochemie*, Vol. 19, 1919, pp. 925–932.

25. Sieverts, A., and Krumbhaar, W., "Solubility of Gases in Metals," *Berichte der deutschen chemischen Gesellschaft*, Vol. 43, 1910, pp. 893–900.

26. Marre, F., "The Fixation of Atmospheric Nitrogen by the Use of Aluminum Nitride," *Genie Civil*, Vol. 61, 1912, pp. 30–33.

27. Dafert, F. W., and Miklauz, R., "Compounds of Cerium With Nitrogen and Hydrogen," *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*, Vol. 33, 1912, p. 911.

28. Muthmann, W., and Kraft, K., "Investigations of Cerium and Lanthanum," *Liebigs Annalen der Chemie*, Vol. 325, 1902, pp. 261–278.

29. Hardtung, H., *Beiträge zur Kenntnis der Metallnitride*, Hanover, 1912.

30. Hartmann, I., Nagy, J., and Jacobsen, M., "Explosive Characteristics of Ti, Zr, Th, U, and Their Hydrides," *Reports on Investigations*, U. S. Bureau of Mines, No. 4835, 1951.

31. Weiss, L., and Kaiser, H., "Über metallisches Titan," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 64, 1910, p. 352.

32. Valensi, G., "The Dissociation of Chromium Azide," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 187, 1928, pp. 293–296.

33. Neumann, B., Kroger, C., and Haebler, H., "The Heat of Formation of the Nitrides. I. Manganese Nitride and Chromium Nitride," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 196, 1931, pp. 65–78.

34. Valensi, G., "The Action of Nitrogen on Manganese," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 187, 1928, pp. 376–378.